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Range and Ionization Measurements on High Speed Protons

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The relative specific ionization along an initially mono-energetic 4-Mev proton beam has been measured. The stopping power of aluminum relative to air is found to be 1.48 mg/cm² per cm of air at 15°C and 76 cm Hg, and is also found to be independent of the energy in the interval from 1.5 Mev to 4.0 Mev. That this should be so is adequately explained in the interpretation by J. A. Wheeler. The stopping power of a variety of metal foils was also measured and the results are given. From the above measurements it is possible to calculate I, the mean excitation energy of atoms with many electrons (a constant which enters in Bethe's formula for the rate of loss of energy of heavy particles due to ionization) to be 0.85 $Z(me^4/2\hbar)$ or 11.5 Z in electron volts.

A. INTRODUCTION

IN connection with an experiment on proton-proton scattering[1] in which the small Berkeley cyclotron (4-Mev protons) was used, it was desirable to obtain a mono-energetic proton beam of known energy. The raw beam of the cyclotron is inhomogeneous in energy by as much as twenty percent.[2] This difficulty was circumvented by appropriately placing three one-mm slits about 30 cm apart and in the fringing magnetic field of the cyclotron.[3] Although this decreased the intensity of the original beam by a factor of about one thousand, there was ample current left for scattering and range experiments. To determine the energy of this so obtained mono-energetic beam, it was decided for reasons of expediency and accessibility to measure the ionization in air produced by the protons as a function of their range. It is felt that the results of these measurements, although terminated before their completion, are of sufficient interest to warrant publication.

B. RELATIVE IONIZATION BY HIGH ENERGY PROTONS

Figure 1 illustrates the apparatus and method of measuring the relative ionization produced by the protons. Because of the difficulty of keeping the beam current constant, it was necessary to use two ionization collectors as shown; one to measure the specific ionization at various points along the proton path, and another, which was kept in a fixed location, to serve as a monitor ion collector. The protons emerge from the vacuum system through a one-half mil Cellophane foil and first pass through the monitor ion collector. Then they pass through air until they reach the movable shallow ion collector. This collector consists of a thin aluminum foil (2.16 mg/cm²) located 0.5 mm in front of an insulated circular

* The experimental part of this paper was done in August, 1940 at the Radiation Laboratory of the University of California.
[1] R. R. Wilson and E. C. Creutz, Phys. Rev. **59**, 916 (1941).
[2] R. R. Wilson J. App. Phys. **11**, 781 (1940).
[3] E. C. Creutz and R. R. Wilson, Phys. Rev. **59**, 916 (1941).

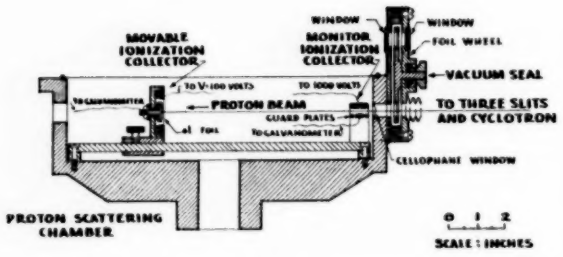

FIG. 1.

brass button of $\frac{3}{4}''$ diameter. The foil was raised to a potential of a few hundred volts with respect to the button, and the ionization current to the button was measured with a sensitive galvanometer. The monitor collector consisted simply of two parallel plates (with guard plates), one of which was raised to a potential of about a thousand volts and the other which led to a galvanometer that measured the ion current. The voltages on the collectors were adjusted high enough so that the ionization currents were very nearly independent of voltage.

The ratio I of the ionization current in the shallow ion chamber to that in the monitor collector, normalized to unity at its maximum value, is plotted in Fig. 2 for various positions of the shallow ionization collector. It is seen that the points fall along a typical Bragg curve. To determine if the results were influenced by heating of the air due to the energy loss of the protons (current about 10^{-10} amp. and of cross section 1×2 mm), a run was made with one-half the proton current used before. Within the accuracy of the measurements, the points were unchanged from their previous values. The temperature of the air as well as the atmospheric pressure was read at each measurement so that the results could be reduced to standard values. Because of multiple scattering in the air, the proton beam, as indicated by the fluorescence it produced on a ZnS screen, spread out to nearly the full aperture of the movable ion collector at its greatest distance from the entrance foil, and it is possible that the points near the end of the Bragg curve are slightly influenced by this effect.

The striking characteristics of the curve are the pronounced decrease of ionization with energy, the very sharp maximum, and the rapid linear decrease of the curve after the maximum. The curve can be fit adequately, except for the last two cm, by an equation of the form

$$I=A/(R_0-R), \tag{1}$$

where A and R_0 are constants with values 4.2 and 27 cm, respectively. The sharp maximum is an indication of how mono-energetic the proton beam was. The intersection of a straight line fitted to the linear part near the end of the Bragg curve with the range axis gives the *extrapolated ionization range*. It can be seen that this quantity is very precisely determined from such an

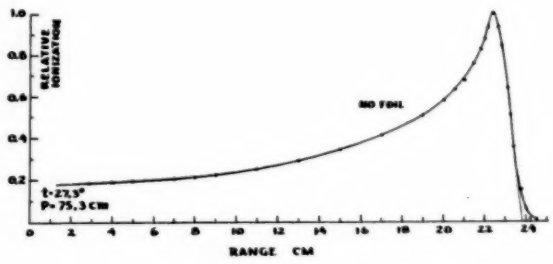

FIG. 2.

ionization range curve. However, the relation between the extrapolated ionization range and the mean range, from which can be obtained the energy,[4] is not yet accurately known for protons. The difference between the two ranges can be calculated if one knows how the ionization varies along the path of an individual proton, especially near the end of the range. Rado[5] has attempted to do this with the available data. Inasmuch as these data are so widely variable from one observer to another, he was unable to reach any definite value. His work does suggest, however, that 0.6 cm should be subtracted from the extrapolated ionization range of 23.2 cm, as read from Fig. 2, to give 22.6 cm as the mean range. When this range is reduced to 15°C and 76-cm Hg pressure, and when the stopping power of the foils is added, we obtain 4.00 Mev for the energy of the protons as given by the Cornell range energy relation.[5] The determination of the stopping power of the foils will be explained in the next section.

It is felt that obtaining an ionization range

[4] M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 264 (1937).

[5] Rado, Thesis, Massachusetts Institute of Technology (1939).

curve would be a convenient and accurate method of determining the energy of a proton beam if a relation between the energy and the extrapolated ionization range existed. It is hoped to obtain such a relation experimentally by using the magnetic analyzer developed at Princeton for measuring proton energy.

C. The Stopping Power of Aluminum and of Other Metals

A rotating foil wheel was located as shown in Fig. 1 so the protons could pass through any one of the several aluminum foils of different thicknesses. The thickness of each foil was determined by measuring its area and weight with an accuracy of about one percent. The area of each foil was about one square cm. A chemical analysis of the aluminum from which the foils was cut showed it to be 99.35 percent aluminum, 0.35 percent iron, and 0.25 percent silicon.[6]

With each foil in place, the same type of measurements were made as described in the previous section. The results of this series of measurements are shown in Fig. 3. All the data were taken at one time. The curves all seem to have the same shape as that obtained with no foil, except that they are shifted to the left. This indicates that the straggling does not differ appreciably in air and aluminum. In Fig. 4 the

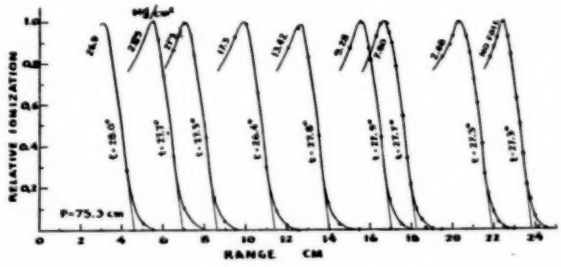

Fig. 3.

stopping power of each foil, determined by subtracting the extrapolated ionization range obtained with the foil from that without a foil, is plotted. The extrapolated ranges were reduced to the same temperature and pressure (300°K and 73.31-cm Hg) before the subtractions were made. Figure 4 shows that the stopping power of each foil when plotted against its weight per mg falls surprisingly close to a straight line that passes through the origin. This is interpreted as meaning that the stopping power relative to air is independent of the energy in the interval from 1.5 to 4.0 Mev. The slope of the straight line of Fig. 4 gives the specific stopping power to be 1.48 mg/cm² of aluminum per cm air when reduced to 15°C and 76 cm Hg.

In the same way, the stopping powers of several other metal foils were measured. In these

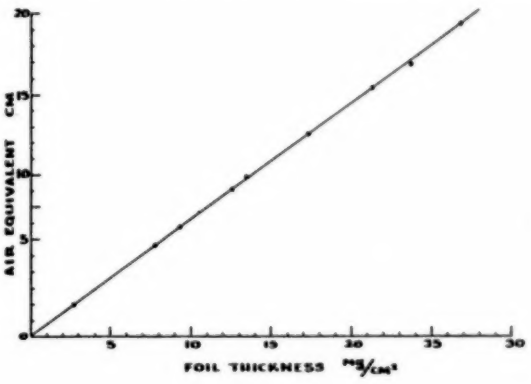

Fig. 4.

cases only one foil of each metal was available. The ionization range curves are shown in Fig. 5, and in Table I is listed the specific stopping power for each of the foils measured and the quantity q which is explained in the interpretation.

D. Interpretation of the Results[7]

Bethe has given a well-known formula[8] for the rate of loss of energy per unit of path length by heavy particles of non-relativistic velocity. For protons his relation reduces to

$$-dE/dx=(4\pi NZe^4/mv^2)\ln(2mv^2/I). \quad (2)$$

Here v is the speed of the particle, and e and m represent the electronic charge and mass, N gives the number of atoms per unit of volume, Z is the atomic number of the stopping material and I is a certain mean excitation energy characteristic of the atom in question. The value of I varies with atomic number in a complicated way for light atoms. On the other hand, for atoms containing many electrons, Bloch has shown[9] on the basis of

[6] The foils and analysis were kindly supplied by the Reynolds Metals Company.

[7] Discussion contributed by J. A. Wheeler.
[8] H. A. Bethe, Ann. d. Physik **5**, 325 (1930).
[9] F. Bloch, Zeits. f. Physik **81**, 363 (1933).

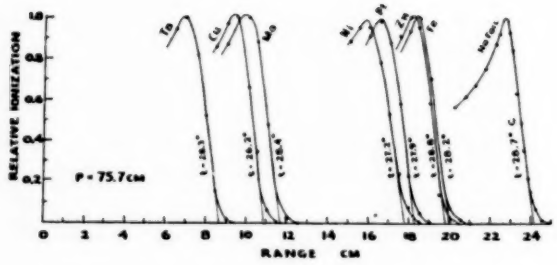

FIG. 5.

the statistical atomic model that the mean excitation energy should be proportional to the atomic number, Z. No one has as yet computed from first principles the constant of proportionality,[10] which therefore has to be found by comparison with experiments. This Bloch did.[9] He found $I/Z=0.961(me^4/2h^2)=13.1$ ev. Unfortunately the velocities at which measurements were available in 1933 were limited to 1.92×10^9 cm/sec. (7.6 Mev alpha-particle; same speed as K electrons of element $Z=9$). In the meantime further theoretical work of Livingston and Bethe[4] has emphasized the importance of the corrections which must be introduced into the simple relation (2) when the velocity of the particle is low enough to be comparable to the speed of the bound electrons in the stopping material. One would arrive at a misleading estimate of Bloch's constant if he were to look apart from such corrections even in discussing the present experiments of Wilson, performed with protons of velocity ranging up to $v=2.77\times10^9$ cm/sec. Thus if Bethe's simple formula applied, and I were exactly proportional to Z, one would expect there to exist a linear relationship between relative stopping power and logarithm of atomic member:

$$\frac{(-dE/NZdx)_{\text{material}}}{(-dE/NZdx)_{\text{air}}}=\frac{\ln(2mv^2/\text{constant})-\ln Z}{\ln(2mv^2/\text{constant})-\ln 7.22}. \quad (3)$$

The left-hand side of relation (3) may be represented by the letter q:

$$q=\frac{(-dE/NZdx)_{\text{material}}}{(-dE/NZdx)_{\text{air}}}=\left[\frac{(NZdx)_{\text{air}}}{(NZdx)_{\text{material}}}\right]_{\text{for equivalent stopping}}=\frac{\text{atomic weight of material}}{\text{twice its atomic number}}\times\left(\frac{\text{mg/cm}^2\text{ of air}}{\text{mg/cm}^2\text{ of material}}\right)_{\text{for equivalent stopping.}} \quad (4)$$

This quantity has been computed from the experimental data in Table I and is plotted in Fig. 6 as a function of $\ln Z$. It is seen that q is a practically linear function of $\ln Z$. Without further consideration one would be led to the false conclusion that he could obtain a fairly accurate value of Bloch's constant from the intercept of the straight line with the horizontal coordinate axis: $\ln(2mv^2/\text{constant})=6.40$, whence $I/Z=$effective mean of initial and final energy of proton, divided by 276,000. Actually, however, the mean energy of the protons employed in the experiments differed considerably (2–4 Mev) from element to element, so that on the basis of Bethe's simple theory one should not expect the points in Fig. 6 to come at all close to a straight line, as they do. Moreover, for a definite element, such as aluminum, the stopping power relative to air is seen from Fig. 4 not to vary with energy as it should according to (3).

Both of the difficulties just mentioned are resolved when one notes that the speed of a K electron of aluminum is 2.8×10^9 cm/sec., or practically equal to that of the proton. This

TABLE I. *Specific stopping power.*

FOIL	$\frac{\text{MG}}{\text{CM}^2}$	TOTAL STOPPING BY FOIL IN CM	SPECIFIC STOPPING POWER IN $\frac{\text{MG}}{\text{CM}^2}$ PER CM	ENERGY INTERVAL IN MEV	q
Al	17.30	11.72	1.48	1.5–4.0	0.864
Cu	25.35	12.55	2.02	2.6–4.0	0.665
Fe	7.47	4.07	1.83	3.7–4.0	0.718
Mo	27.85	11.87	2.34	2.7–4.0	0.597
Ni	11.48	5.97	1.92	3.4–4.0	0.668
Pt	17.80	5.40	3.30	3.4–4.0	0.465
Ta	47.20	14.72	3.20	2.2–4.0	0.475
Zn	8.29	4.13	2.01	3.7–4.0	0.668

[10] An approximate theoretical estimate was, however, made by H. Jensen, Zeits. f. Physik **106**, 620 (1937).

circumstance requires the introduction of the corrections of Livingston and Bethe[4] into the right-hand side of (3), which then, quite independent of Bloch's theory of excitation energies, becomes:

$$\frac{\ln(2mv^2/I_{\mathrm{Al}})-(C_k/Z)_{\mathrm{Al}}}{\ln(2mv^2/I_{\mathrm{air}})-(C_k/7.22)_{\mathrm{air}}}. \tag{5}$$

For I_{air} Livingston and Bethe find 80.5 ev or $5.92(me^4/2\hbar^2)$ from the observed absolute stopping power.[4] Their Fig. 28 gives the corrections C_K. Wilson's Fig. 4 shows that 27.8 mg/cm² of Al are equivalent to 20 cm air (300°K, 75.31 cm pressure). This comparison gives for the ratio (5) the value $(26.97/26)(20\times1.166/27.8)=0.870$, constant over the range of velocities investigated. These data are used in Table II to compute I_{Al}.

The values in the last column come out to be strikingly consistent with one another. Since corrections for binding of the L electrons will be least important at the higher energies, it is reasonable to take 8.83 as best value of $\ln(2mc^2/I_{\mathrm{Al}})$. This result gives $I_{\mathrm{Al}}=150$ ev $=11.0(me^4/2\hbar^2)$. Table II suggests why the stopping power of aluminum is constant relative to air over a considerable interval of energy: the correction for binding of the K electrons is decreasing for one element, increasing for the other. The complicated nature of the compensation shows how difficult it is to give any simple interpretation to the linear relationship in Fig. 6.

TABLE II. *Determination of mean excitation energy of aluminum from stopping power relative to air observed by Wilson for protons of various energies.*

Energy Mev	$\ln(2mc^2/I_{\mathrm{air}})$	$(C_k/7.22)_{\mathrm{air}}$	Numerator of (5)	$(C_k/Z)_{\mathrm{Al}}$	$\ln(2mc^2/I_{\mathrm{Al}})$
2.0	4.00	0.11	3.38	0.04	8.87
2.5	4.22	0.10	3.58	0.05	8.86
3.0	4.40	0.10	3.73	0.05	8.83
3.5	4.55	0.09	3.87	0.06	8.83
4.0	4.69	0.08	4.00	0.06	8.82

As basis for fixing the constant of proportionality between I and Z there is really available at present only the data for air and aluminum:

Air, $I/Z=11.15$ ev $=0.820(me^4/2\hbar^2)$,
Aluminum, $I/Z=11.54$ ev $=0.848(me^4/2\hbar^2)$.

Since Bloch's statistical theory of the proportionality is the more nearly correct the higher is the atomic number, it seems to be reasonable in the light of the evidence to write for the mean excita-

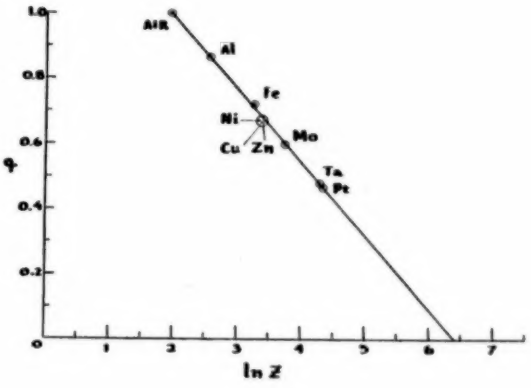

FIG. 6.

tion energy of atoms with many electrons

$$I/Z=11.5 \text{ ev}=0.85(me^4/2\hbar^2).$$

The constant in (6), about 10 percent lower than that given by Bloch, is employed in the following paper to determine the range-energy relation for fast particles in lead.

In conclusion the author takes pleasure in expressing his gratitude to Professor Ernest O. Lawrence for the privilege of using the cyclotron. I am especially grateful to Professor John A. Wheeler for pointing out the importance of the measurements and for contributing the interpretation. Acknowledgment is made to the Research Corporation for financial support in this project.

Mass of the Meson by the Method of Momentum Loss

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Observations on the curvature of the track of a meson before and after traversal of a known amount of matter allow a determination of the mass of the particle. A discussion is presented of the accuracy and advantages of this method of measuring mass, the principle of which is well known but has so far been little used. In this connection the stopping power for fast particles has been computed on the basis of the experiments reported by R. R. Wilson in the preceding paper. Discussion of the formula used is contained in the appendix. Curves are presented for the dependence of range on energy and momentum for swift hydrogen and helium nuclei as well as for mesons. The method of momentum loss is illustrated and values are obtained for the mass of the meson from measurements published by Anderson and Neddermeyer in 1934. The evidence available from these mass determinations and those published by other authors shows the necessity for many more mass determinations before one can decide whether there is a distribution of masses of the meson or not.

INTRODUCTION

MEASUREMENT of the range of a meson and of the curvature of its track by a magnetic field, i.e., its momentum, are well known to suffice for a determination of its mass. For this purpose use is made of the theoretical relation between initial momentum and total path length. In a variant of this method one applies the differential form of the momentum-distance relation, and measures the change in magnetic rigidity of the particle over a small portion of its path. This procedure has been employed by several observers, and Corson and Brode[1] have discussed it in some detail.

The longer is the segment of path length considered, and the higher is the atomic number of the traversed material, the more surely one can exclude the possibility that the particle in question is an electron. But then one can no longer directly apply the differential expression for the rate of change of momentum with distance. Still it is in principle possible also in this case to determine the mass of the particle, as Neddermeyer and Anderson[2] remark in a recent review of methods of measuring this quantity. From an experimental point of view it is only necessary to observe the curvature before and after traversal of a plate of known thickness. However the procedure in question has been but slightly used.

This way of determining mass by the method of momentum loss appears to deserve further emphasis for three reasons:

(a) The necessary measurements of curvature of track in a magnetic field and of thickness of material traversed are among the most direct in the whole field of cosmic-ray research. Difficult determinations of the density of ionization along the track are avoided.

(b) Accuracy in this method, as in almost all other methods of determining the mass, requires that the velocity of the meson be not close to the speed of light. In the acceptable range of velocities, however, practically every meson whose curvature can be measured before and after penetration of the plate will permit an evaluation of its mass. Contrast this attainable abundance of data with the rarity of those collisions of a meson with an electron in which the energy transfer is sufficient to allow a determination of mass from the laws of conservation of momentum and energy.

(c) The law for the stopping power of matter for fast particles has an exceedingly reliable theoretical basis.[3]

The question whether all mesons have the same mass is so important that it appears worth while to give a qualitative discussion of the

[1] D. R. Corson and R. B. Brode, Phys. Rev. **53**, 776 (1938).

[2] S. H. Neddermeyer and C. D. Anderson, Rev. Mod. Phys. **11**, 200 (1939).

[3] See in this connection E. J. Williams, Phys. Rev. **45**, 729 (1934).

resolving power of the "method of momentum loss." If the energy of the meson is large in comparison with its rest energy, the loss of energy, ΔE, in a given thickness of material will be practically independent of energy, according to the theory of stopping power. In the relativistic relation between losses of energy and momentum, $\Delta E \sim v dp$, the velocity v will be essentially a constant, the speed of light. We will therefore find fast particles losing momentum of the same order of magnitude whatever be their mass. Consequently the resolving power is poor for mesons of relativistic velocity (momentum $\gg$100 Mev/c; $H\rho \gg 4\times 10^5$ gauss cm).

This insensitivity of the momentum loss at relativistic velocities to the mass of the particle conversely makes it possible to test the law of stopping even for mesons whose precise masses are unknown. It is only necessary that their energies be sufficiently great: $H\rho > 10^6$ gauss cm. Measurements under this condition of the change in curvature on traversal of a plate were made by J. G. Wilson[4] and were found to verify a theoretical expression for the absolute rate of loss of energy not very different from (1) below.

For non-relativistic speeds the rate of energy loss per unit of distance may be written very roughly in the form

$$dE/dx \sim \text{constant}/v^2.$$

From this it follows that the mass, μ, of the particle is given by

$$\mu \sim p(dp/\text{const. } dx)^{\frac{1}{2}}.$$

The percentage error in μ will be given by the sum of (a) the percentage error in the momentum, p, or corresponding magnetic rigidity, $H\rho$, of the particle; (b) one-third the percentage error in the measurement of the momentum loss (if that loss is small compared to p); (c) one-third the percentage error in the thickness of the stopping material; (d) one-third the percentage error in the theoretical constant of the stopping power formula.

These considerations on the whole favor the "method of momentum loss" for non-relativistic velocities.

[4] J. G. Wilson, Proc. Roy. Soc. **A172**, 517 (1939).

Range-Momentum Relation

A more complete treatment of the method in question requires a discussion of the law of stopping power. Fortunately, radiative losses can be neglected for mesons of much greater than electronic mass as for protons and alpha-particles, even for the highest velocities ($v=0.9c$) and greatest atomic numbers (Pb; $Z=82$) which will be of interest. The so-called "radiation unit" or "unit length" of the radiative theory will have a value for mesons greater than that for electrons (0.4 cm in the case of Pb) approximately in the ratio of the squares of the two masses. Thus the mean energy dE_r lost in the form of radiation by a meson of 150-Mev energy and of mass 200 m traversing 1 cm of lead will be given by[5]

$$dE_r/E \sim dE_r/150 \text{ Mev} \sim (1 \text{ cm}) \ln 2/(200)^2\, 0.4 \text{ cm},$$

whence $dE_r \sim 0.01$ Mev. This value is trifling in comparison with the loss of $\sim$10 Mev by ionization, which alone therefore need be considered.

According to the theory of stopping power, the rate of dissipation of energy through ionization and excitation by a fast particle of velocity v and of not too great charge number, z, will be given by the relation,[6]

$$dE/dx = (4\pi N e^4 z^2/mv^2) \times \{\ln[2mv^2/I(1-v^2/c^2)] - (v^2/c^2)\}. \quad (1)$$

Here N represents the number of electrons per cm^3 of stopping material, I is a certain mean energy of excitation for these electrons and m is the electronic mass. For atomic hydrogen,[7] $I = 1.103(me^4/2\hbar^2)$; for helium,[8] $I = 3.19(me^4/2\hbar^2)$. For air ($Z=7.22$), Livingston and Bethe[9] determined the mean excitation energy from the observed stopping power: $I = 5.92(me^4/2\hbar^2)$. The experiments of R. R. Wilson reported in the preceding paper permit a similar evaluation of the mean excitation energy for aluminum:[10] $I = 11.02(me^4/2\hbar^2)$. Elements of high atomic num-

[5] For a more detailed treatment of the radiation loss, see H. J. Bhabha, Proc. Roy. Soc. **A164**, 257 (1938).
[6] For literature and discussion see Appendix.
[7] H. A. Bethe, Ann. d. Physik **5**, 325 (1930).
[8] E. J. Williams, Proc. Camb. Phil. Soc. **33**, 179 (1937).
[9] M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 267 (1937).
[10] R. R. Wilson, Phys. Rev. **60**, 749 (1941) and discussion at end of Wilson's paper by J. A. Wheeler.

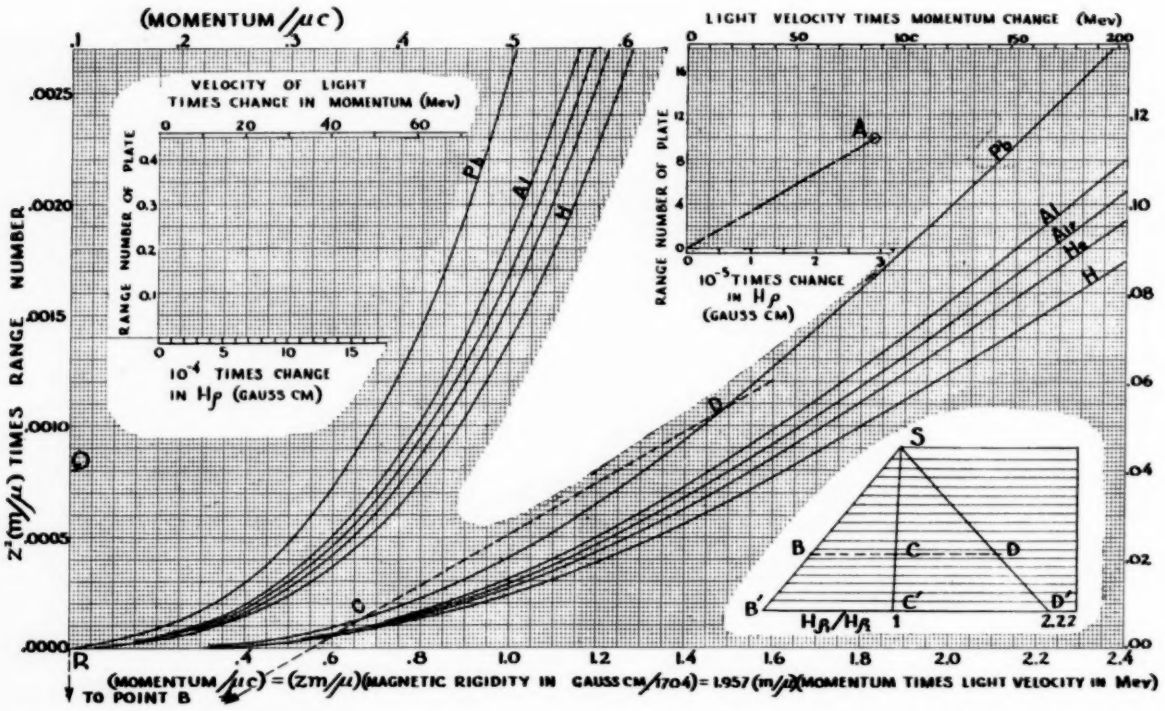

FIG. 1. Calculated relation between range and momentum for hydrogen and helium nuclei and for mesons. For the stopping materials computations were based on values of the mean ionization energy mentioned in the text. For Pb and Al the ionization energy was determined from Bloch's formula with the constant of proportionality based on the data of R. R. Wilson in the preceding paper. To interpolate for the stopping power of a compound substance such as $PbCl_2$ note that the logarithm of the effective atomic number is $(82 \ln 82 + 34 \ln 17)/(82+34)$. Given that a meson ($z=1$) with a given magnetic rigidity, $H\rho$, of 528,000 gauss cm passes through a 3.70-cm lead plate, corresponding to a range number of 9.92, and emerges with a rigidity of 238,000 gauss cm. We compute the change in $H\rho$ and plot the point A in the upper diagram. The secant CD must be parallel to OA but the positions of C and D individually remain to be found. A large scale transparent model is constructed of the template in the lower right corner of the figure. Lines SC and SD are drawn such that $D'B' : C'B' = DB : CB = 528{,}000$ gauss cm: 238,000 gauss cm. $= 2.22$. With its rulings parallel to OA and with corresponding points $C'D'$ or CD, etc., kept on the curve for lead, the template is moved until the prolongation B' of $C'D'$ or B of CD, etc., lies on the line QR extended. The graphical solution so found is indicated by the points CD on the range curve. From the location of D it is seen that $1.49 = (m/\mu)(H\rho_1/1704) = 310\ (m/\mu)$. This result gives $\mu = 209\ m$ for the mass of the meson as determined from the given observations.

ber are most effective in distinguishing mesons from electrons in the method of momentum loss, but for these no direct determination of the mean excitation energy is available. Fortunately (a) the stopping power is not very sensitive to the value of I and (b) Bloch's theory of excitation energies[11] permits a satisfactory estimate of this quantity. According to Bloch, the mean excitation energy for atoms containing many electrons is proportional to the atomic number Z. For the constant of proportionality he gave the value $I/Z = 0.96(me^4/2\hbar^2) = 13.1$ ev on the basis of the experiments available in 1933, but the data reported in the preceding paper by Wilson lead to a more reliable estimate of Bloch's constant:[10]

$$I/Z = 0.85(me^4/2\hbar^2) = 11.5 \text{ ev}.$$

[11] F. Bloch, Zeits. f. Physik **81**, 363 (1933).

For atoms to which the Thomas-Fermi model applies this formula gives

$$\ln(2mc^2/I) = 11.391 - \ln Z. \qquad (2)$$

Let us now state the connection between range and energy or momentum in the form which is convenient for general use and at the same time suited for determining the mass of the meson. The range of a particle of mass μ and charge number z may be considered to depend on any one of the following quantities:

$$\begin{aligned} &\text{kinetic energy:} && E = \mu c^2(\cosh\theta - 1) \\ &\text{momentum:} && p = \mu c \sinh\theta \\ &\text{magnetic rigidity:} && H\rho = \mu(c^2/ze)\sinh\theta \\ &\text{velocity:} && v = c\tanh\theta. \end{aligned} \qquad (3)$$

Better than any of these quantities for inde-

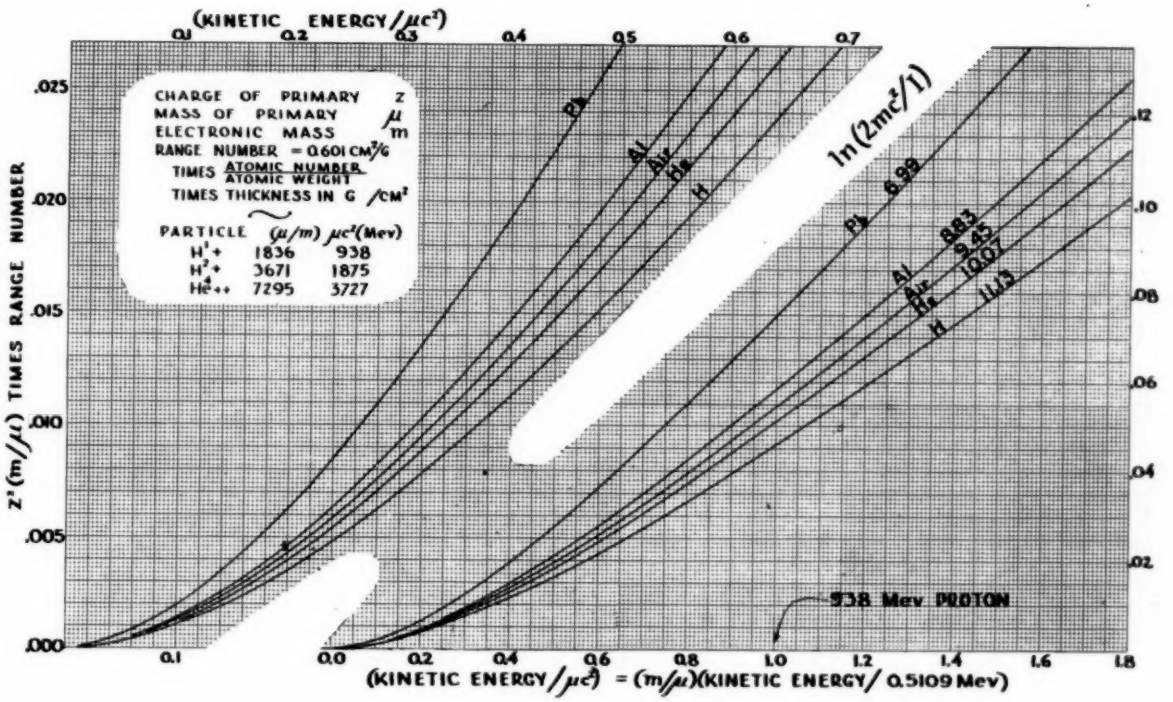

FIG. 2. Calculated relation between range and energy for hydrogen and helium nuclei and for mesons. The point x corresponds to an alpha-particle with the following properties: energy = 0.2×3727 = 745 Mev; range in aluminum = 0.0046 ×(7295/4)×(26.97/13×0.601 cm²/g) = 29 g/cm² or 10.7 cm.

pendent variables, however, are the dimensionless numbers $\sinh\theta$ and $\cosh\theta$, used in Figs. 1 and 2, respectively. If the dependent variable or range is expressed in g/cm² it will fluctuate in an irregular way from element to element because of the lack of any precise relation between atomic number Z, and atomic weight, A. For this reason let us express the range in terms of a dimensionless "range number," defined as follows:

$$\begin{aligned}\text{"range number"} &= 4\pi\cdot\text{Avogadro's number}\\ &\cdot(e^2/mc^2)^2\cdot(Z/A)\cdot(\text{range in g/cm}^2) \qquad (4)\\ &= (0.601\ \text{cm}^2/\text{g})\cdot(Z/A)\cdot(\text{range in g/cm}^2).\end{aligned}$$

In the case of CH_4, the expression Z/A will have the value $(6+4)/(12+4)$. In the case of dry air at 15°C, at a pressure of $76\times13.6\times980$ dynes/cm², division of the range by 2714 cm gives the range number. For lead of density 11.3 g/cm³ range number equals thickness multiplied by 2.68 cm^{-1}.

In terms of the "range number," relation (1) takes the form $(z^2m/\mu)\cdot(\text{range number}) =$

$$\int^{\theta}\frac{d(\cosh\theta+\cosh^{-1}\theta-2)}{\ln(2mc^2/I)+2\ln\sinh\theta-\tanh^2\theta}. \qquad (5)$$

Numerical integration gives the curves[12] drawn in Figs. 1 and 2. The constant of integration was fixed in the case of air so as to give a range of 238 cm for 15 Mev protons;[9] it was estimated in the case of the other substances listed. Negligible on the scale of the figures is the slight dependence of the constant of integration in (5) upon the charge of the primary, a dependence which arises principally from the phenomenon of capture and loss of electrons at the very end of the range. Of course, the constant of integration has no effect on the determination of the mass of the meson by the method of momentum-loss.

Figure 1 illustrates how measurements of magnetic rigidity before and after a meson

[12] As long as they last, large photostats of these curves may be obtained from the Secretary, Department of Physics, Princeton University. We are indebted to Mr. Ralph Thompson for much help with the numerical computations.

TABLE I. *Columns 1, 2 and 3 give measurements of Anderson and Neddermeyer on single cosmic-ray particles. On the preliminary assumption that each particle is a meson, the range-momentum relation allows as described in Fig. 1 a computation of the ratio (μ/m) of unknown mass to electronic mass. Knowledge of the mass and momentum after traversal of the lead plate suffices to determine the factor $1/\beta^2 = (\text{velocity of light/velocity of particle})^2$ which is approximately proportional to the ionization. It is seen that this ionization would be exceedingly large for the last three particles if they were mesons. However, the observed rate of ionization, according to a kind personal communication of Anderson, is certainly not so great for these particles as twice the rate for a fast electron. Therefore the last three particles cannot be mesons of the computed masses. In the absence of information about the ionization of the other particles, we have calculated the "energy decrement number," I, to test whether it is reasonable to assume that these particles are electrons which have experienced radiative losses. According to theory, all values of I between 0 and 1 are equally probable for electrons. Consistently small values of I are therefore an argument against attributing electronic character to a group of particles. The angles θ* elec. *and θ* meson *are defined in the text. Arguments based on scattering indicate that no one of the last five tracks, even if it represents a meson, will permit a mass determination.*

1 Thickness of Lead	2 Momentum cp_1 (in Mev)	3 Momentum cp_2 (in Mev)	4 E_t (Mev)	5 Analysis if Electron t	6 Analysis if Electron I	7 θ Elec. (Degrees)	8 $c\Delta p$ (Mev)	9 Range Number	10 Anlaysis if Meson $\frac{H\rho_1}{H\rho_2}$	11 Anlaysis if Meson $\frac{\mu}{m}$	12 $\frac{1}{\beta^2}$	13 θ Meson (Degrees)
1.35	113	86	102	3.1	0.00	33	27	3.6	1.32	150	1.8	44
1.1	220	160	173	2.5	0.01	16	60	3.0	1.33	590	4.6	35
1.1	200	125	138	2.5	0.02	21	75	3.0	1.60	560	6.2	52
1.1	240	220	233	2.5	0.00	12	(20)	3.0	1.09	(310)	1.5	14
1.1	38	6	19	2.5	0.07	430	32	3.0	6.3	[45]	15.7	1700
0.7	63	23	31	1.6	0.27	90	40	1.9	2.7	[110]	6.9	238
1.0	140	20	32	2.3	0.34	123	120	2.7	7.0	[390]	101	1230
1.0	106	26	38	2.3	0.20	95	80	2.7	4.1	[250]	26	475
1.5	110	12	30	3.5	0.09	250	98	4.0	9.2	[220]	88	2350

penetrates a plate of known thickness allow a determination of the mass of the meson.

Distinction Between Electrons and Mesons

In 1934 Anderson and Neddermeyer[13] reported measurements on the momentum loss of single cosmic-ray particles which had traversed ~1 cm of lead without undergoing multiplication. Their observations are reproduced in the first three columns of Table I. As the cascade theory and the work of these and other physicists have since emphasized, many particles of this character at sea level are mesons. On the preliminary assumption that all of the particles are mesons, the entries in column 8 of Table I will represent loss of momentum by ionization alone. Consequently the methods outlined in the caption of Fig. 1 will permit a determination of the mass of each particle. The values in columns 8, 9, and 10 of the table were used in the graphical calculations. The computed ratio of the mass of each particle to that of the electron is given in column 11. No estimate of probable error has been attempted. Those values will generally be the more reliable where the fractional loss in momentum has been the greater.

From the data alone it is not possible to tell which tracks represent mesons and which represent electrons. In fact two possible explanations exist for the change in momentum in any given instance. Either the loss is due to a high rate of ionization, in which case the particle must be moving slowly, and the quotient (momentum/velocity) will be large and will indicate a meson; or the loss is due to radiation, which is only possible if the mass is comparable to that of an electron. There are in principle, however, three qualitative means to distinguish between electrons and mesons: (a) ionization, (b) scattering, and (c) the theory of radiation.

(a) A meson emerging from the lead plate into the cloud chamber will ionize more than an electron of the same momentum. The relative rate of ionization will be given approximately by the ratio $c^2/v^2 = 1+(\mu c^2/cp)^2$ which has been computed in column 12 of Table I on the assumption that the particles are mesons. The calculated rates of ionization are on the whole rather different from those to be expected for electrons, and in fact Dr. Anderson informs us that an inspection of the last three tracks shows that

[13] C. C. Anderson and S. H. Neddermeyer, *International Conference on Physics* (London, 1934, Table II, p. 179).

this criterion excludes the possibility that these tracks represent mesons. It will be noted that this test requires only a qualitative knowledge of the ionization, in contrast to those methods of determining the meson mass which depend on an accurate count of numbers of ions.

(b) Particles of the same momentum will suffer the more scattering the greater is their mass. Following the treatment of multiple scattering given by Williams,[14] we may express the arithmetic mean projected angle of deflection due to multiple scattering in lead approximately in the form

$$\theta \text{ in degrees} = (2500 \text{ degrees Mev}/pc).\ (\text{thickness in cm})^{\frac{1}{2}}(1+[\mu c^2/pc]^2)^{\frac{1}{2}}. \quad (6)$$

Here there is some ambiguity as to the proper mean value to insert for the momentum, p, which changes in traversing the plate. The scattering is greatest when the particle is traveling most slowly. We have used for p in (6) the momentum after traversal of the plate in order to obtain a rough estimate of the order of magnitude of the scattering to be expected for each of the tracks in Table I. As columns 7 and 13 of this table show, there is not sufficient difference in the expected scattering for the first four particles to distinguish between electrons [$\mu = m$ in Eq. (6)] and mesons (μ from column 11 of table). For the last five tracks the computed scattering is so great that the calculation itself has no meaning. It is clear that these tracks will give no information about the mass of mesons.

Generalizing the foregoing conclusion, we may say that it is important to avoid large scattering in determining the mass of the meson by the method of momentum loss. This condition will be satisfied if the momentum of the particle after traversal of the plate is not too small. On the other hand, the momentum afterward must be considerably less than that before traversal if the measurement of the momentum change is to be accurate. Both conditions will be abundantly fulfilled if the primary momentum is of the order of 100 Mev and the momentum decreases in the plate by a factor of the order of 2.

(c) In addition to ionization and scattering as criteria in selecting acceptable tracks, we have in the theory of radiation a means to analyze the possibility that the particles in Table I are fast electrons. If this is the case, they will have lost energy by ionization at a rate of ~ 12 Mev per cm of lead. We can therefore correct the values, cp_2, of the final energy to obtain the value, E_t, which would have been observed if radiative losses alone occurred. Column 4 of the table gives E_t and column 5 shows the thickness, t, of the plate as measured in terms of the so-called "unit-length" of the theory of radiation. There is to be expected a statistical connection between E_t and t. According to Bethe and Heitler[15] the chance, dN, that an electron emerges from the plate with a final energy E_t (corrected for ionization losses) is given by the expression

$$dN = E^{-1}dE_t(\ln E/E_t)^{t-1}/(t-1))! \quad (7)$$

Let us measure the loss of energy through radiation by an "energy decrement number," I, defined as follows:

$$I = \int^{\ln(E/E_t)} y^{t-1}\exp(-y)dy/(t-1)! = I(\ln E/E_t, t-1). \quad (8)$$

This quantity will be zero if there is no energy loss, unity if the particle loses all of its energy by radiation. It is a purely *experimental* quantity and is easily computed, for extensive tables of the function $I(z, p)$ are available.[16] In terms of the "energy decrement number," relation (6) takes a very simple form:

$$dN = dI. \quad (9)$$

In words, *all values of the energy decrement number between zero and unity are equally probable*, whatever be the original energy of the electron or the thickness of the plate which it penetrates.

The energy decrement number, I, for each particle in Table I has been computed according to the definition in Eq. (7). The entries in column 6 show that the values of I are on the whole quite small, particularly for the first four tracks. In the absence of other information, consistently small values of I will be an argument against attributing electronic character to a group of particles.

[14] E. J. Williams, Phys. Rev. **55**, 303 (1940).

[15] H. Bethe and W. Heitler, Proc. Roy. Soc. **A146**, 83 (1934).

[16] K. Pearson, *Tables of the Incomplete Γ-Function* (London, 1922).

TABLE II. *Previously published data on the mass of the meson. The methods used for the determination are: curvature in a magnetic field and ionization density (c and i), curvature and range (c and r), change of curvature in a known amount of matter (c and c), curvature and collision with an electron (c and e). The errors given for the momentum and the mass are those calculated by the authors. The references are listed separately. Notes give additional information from original paper.*

	cp (IN MEV)	MASS (μ/m)	METHOD	REF.
1	33	220 ± 50	c and i	1
2	55	$>430(<800)$	c and i	1
3	44	190 ± 60	c and i	1
4	34	160 ± 30	c and i	1
Note: Values of 1, 3 and 4 are considered reliable; the upper limit of μ/m for particle 2 is set by a minimum range equal to the observed length of track in the chamber, the lower limit is estimated from the lower limit of ionization.				
5	45	250	c and i	2,3
Note: Mass value considered as "good."				
6	29	~130	c and i	4
Note: Value only approximate. Corson and Brode, (3), calculate $\mu/m=160$ with a different method for evaluating the ionization loss.				
7	57	~200	c and i	5
Note: Value "probable," but not very good.				
8	16.5	<200	c and r	14,3
Note: Observable range was 18 cm, track out of focus, so that ionization density not measurable; if it was 10 times normal, mass would be 125.				
9	16.5	~350	c and r	6,3
Note: Observed by (6), calculated by (3); according to private communication from Anderson curvature is average value over whole length of track (4 cm), particle besides probably scattered, computed value has "not much meaning."				
10	$\leqq42$	<1000	c and r	6,3
Note: The same critical remark *a fortiori*, as the particle does not stop in the chamber (range >5 cm) and the $H\rho$ value given is only an upper limit.				
11	52	220 ± 35	c and r	7,8
Note: Considered by Anderson as reliable measurement.				
12	180	<65	c and e	8
Note: Value calculated from *possible* collision with an atomic electron which coming out of the plate shows an energy of 16 Mev; other interpretation possible.				
13	7.7	120 ± 30	cc	9,3
Note: Curvature of track changes in the gas by 0.6 cm/cm. Observed length of 5 cm sets a lower limit for the range which gives according to (3) an upper limit of mass as 110 m.				
14	$222\pm3\rightarrow150\pm3$	180 ± 20	cc	10
Note: Particle loses momentum by penetrating 4.8 cm of Pb; calculated by use of Bhabha's relativistic formula [Proc. Roy. Soc. **A164**, 255 (1938)].				
15	11.6 ± 0.2	170 ± 8	c and r	10
Note: Radius of curvature is an average over range of 6.5 cm, therefore calculated mass is somewhat doubtful, in spite of small margin of error given. No allowance made for the scattering which is important at such a low velocity.				
16	2.4	20?	c and r	11
17	8 ± 3	100 ± 30	c and r	11
18	8.5 ± 1.5	120 ± 30	c and r	11
19	4 ± 2	55 ± 35	c and r	11
20	12 ± 6	$170+100$	c and r	11
Note: Values obtained by use of "slow" cloud chamber; masses of particles 17 and 18 considered as better values than those of the other particles. No allowance made for the scattering which is important at such low velocities.				
21	93	240 ± 20	c and e	12
Note: Value reliable.				
22	$221\rightarrow126$	250 ± 50	cc	13
23	$165\rightarrow87$	170 ± 20	cc	13
Note: 23 considered reliable.				
24	30	180 ± 25	c and i; c and e	15
Note: Reliable.				
Average of reliable values: 180				

[1] E. J. Williams and E. Pickup, Nature **141**, 648 (1938).
[2] D. R. Corson and R. B. Brode, Phys. Rev. **53**, 215 (1938).
[3] D. R. Corson and R. B. Brode, Phys. Rev. **53**, 773 (1938).
[4] J. C. Street and E. C. Stevenson, Phys. Rev. **52**, 1003 (1937).
[5] P. Ehrenfest, Jr., C. R. Paris, **206**, 428 (1938).
[6] C. D. Anderson and S. H. Neddermeyer, Phys. Rev. **50**, 263 (1936), (Figs. 12 and 13).
[7] S. H. Neddermeyer and C. D. Anderson, Phys. Rev. **54**, 88 (1938).
[8] S. H. Neddermeyer and C. D. Anderson, Rev. Mod. Phys. **11**, 191 (1939), (Fig. 19).
[9] A. J. Ruhlig and H. R. Crane, Phys. Rev. **53**, 266 (1938).
[10] Y. N. Nishina, M. Takeuchi and T. Ichimiya, Phys. Rev. **55**, 585 (1939).
[11] H. Maier-Leibnitz, Zeits. f. Physik **112**, 569 (1939).
[12] L. Leprince Ringuet, S. Gorovdetzky, E. Nageotte and R. Richard-Foy, Phys. Rev. **59**, 460 (1941).
[13] J. G. Wilson, Proc. Roy. Soc. **A172**, 521 (1939).
[14] R. B. Brode and M. A. Starr, Phys. Rev. **53**, 3 (1938).
[15] Donald J. Hughes, Phys. Rev. **60**, 414 (1941).

MASS OF THE MESON

The criteria of ionization and scattering exclude the last five tracks in Table I, and the change of momentum is too small for the fourth track to permit a reliable mass determination. Without a qualitative knowledge of the ionization we cannot exclude the otherwise unlikely possibility that the first three tracks represent electrons. If they represent mesons, however, they by no means lead to a unique value for the mass of the meson. Nor do the mass determinations previously published and compiled in Table II allow a decision of the very important question whether the mass of the meson is unique. In this connection we may recall the remark of Anderson and Neddermeyer in 1939[2] that "it has become increasingly likely that a complete interpretation of the experimental data is not to be found in

the single assumption of unstable particles with unit charge and a unique mass of the order of 200 electron masses." Also Weisz[17] has pointed out that assumption of a suitable distribution of meson masses allows a reasonable correlation of otherwise discordant estimates of the lifetime of the meson.

Before any statistically reliable conclusions about the uniqueness of mesons are possible, it will be necessary to obtain many more measurements of the masses of penetrating particles. For this purpose the method of momentum loss appears especially satisfactory in view of the considerations presented in this paper.

We are indebted to Dr. Carl D. Anderson for correspondence and to Dr. Marcel Schein for a number of interesting discussions on the properties of the meson.

Appendix. Remarks on Eq. (1) for Stopping Power

The non-relativistic form of relation (1) was first derived by H. Bethe,[18] who has also given the above relativistic formula. Equation (1) does not, however, agree with the relativistic expressions for stopping power as published in various general references.[19] In the derivation one classifies the various energy losses, Q, into two groups according as they are less than or greater than a certain quantity, Q_1, which is small in comparison to mc^2, large in comparison with atomic binding energies, but which is otherwise arbitrary. The rate of loss of energy by collisions in the first group is

$$(2\pi Ne^4Z^2/mv^2)\{\ln[2mv^2Q_1/I^2(1-v^2/c^2)]-(v^2/c^2)\}$$

as Møller[20] and Bethe[20] have both proven. E. J. Williams[21] obtained the same result by the method of impact parameters and was able to show that the relativistic terms in this expression arise from the Lorentz contraction of the field of the primary particle in distant collisions, and should therefore be considered as especially reliable. In collisions of the second group where the energy transfer is large ($Q>Q_1$) and lies between Q and $Q+dQ$, the calculated average rate of loss of energy is

$$(2\pi Ne^4Z^2/mc^2)(dQ/Q)[c^2/v^2-(Q/Q\ \max)+\text{correction}].$$

Here $Q\ \max=2mp_0^2/(m^2+\mu^2+2mE_0/c^2)$ is the maximum loss which a primary of momentum p_0 and total energy E_0 can experience in a single encounter. The calculated value of the correction term is in general very large and depends in a striking way upon the spin and magnetic moment assumed for the heavy particle.[22] The calculated correction term is however negligible if the energy of the struck electron in the center-of-gravity frame of reference is small in comparison with mc^2. This condition is satisfied if the energy of the primary in the laboratory frame of reference is small in comparison with $(\mu/m)\mu c^2$, or consequently Q max is considerably less than E_0. Then impacts for which Q is between Q_1 and Q max result in an average rate of loss of energy,

$$(2\pi Ne^4Z^2/mv^2)\{\ln(Q\ \max/Q_1)-(v^2/c^2)\}.$$

If in addition μ is much greater than m, then Q max will be given by $2mp_0^2/\mu^2=2mv^2/(1-v^2/c^2)$, and the total average rate of loss of energy will be represented by expression (1). Relation (1) is valid only if the primary is considerably heavier than an electron; only if its energy is small in comparison with $(\mu/m)\mu c^2$; only if it is moving faster than the bound electrons of the stopping material;[23] only if capture and loss of electrons by it can be neglected and its charge is not too great;[24] only if the energy is not so great that the density of the material has an influence upon its stopping power;[25] only if the average energy loss and most probable energy loss are essentially identical.[26] All these conditions are satisfied in the present application.

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[17] P. Weisz, Phys. Rev. **59**, 845 (1941).

[18] H. Bethe, Ann. d. Physik **5**, 325 (1930); *Handbuch der Physik* (1933), second edition, Vol. 24, Part I, p. 523, Eq. (56.16).

[19] Mott and Massey, *The Theory of Atomic Collisions* (Oxford, 1933), p. 269; Heitler, *The Quantum Theory of Radiation* (Oxford, 1936), p. 218; Livingston and Bethe, Rev. Mod. Phys. **9**, 263 (1937), Eq. (750); Neddermeyer and Anderson, Rev. Mod. Phys. **11**, 199 (1939).

[20] Møller, Ann. d. Physik **14**, 579 (1932); Bethe, Zeits. f. Physik **76**, 293 (1932).

[21] E. J. Williams, Proc. Roy. Soc. **A139**, 175 (1933).

[22] H. J. Bhabha, Proc. Roy. Soc. **A164**, 257 (1938); H. S. W. Massey and H. C. Corben, Proc. Camb. Phil. Soc. **35**, 463 (1939); H. C. Corben and J. Schwinger, Phys. Rev. **58**, 953 (1941); W. Pauli, Rev. Mod. Phys. **13**, 230 (1941), Table II.

[23] M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 265 (1937), Eq. (758).

[24] F. Bloch, Ann. d. Physik **16**, 285 (1933); N. Bohr, Phys. Rev. **59**, 270 (1941).

[25] E. Fermi, Phys. Rev. **57**, 485 (1940).

[26] N. Bohr, Phil. Mag. **30**, 581 (1915); C. Møller, Ann. d. Physik **14**, 531 (1932).

An Investigation of the Scattering of Positive Alkali Ions at an Angle of 90° in Mercury Vapor

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The present work is a study of the behavior of potassium, rubidium, and cesium ions emitted from a solid block of Kunsman catalyst, scattered at an angle of 90° in mercury vapor and collected on a stationary cylinder. The values of the incident and scattered currents were measured simultaneously. The incident beam used was of the order of several times 10^{-9} ampere, while the scattered beam was of the order of 10^{-4} to 10^{-3} part of that value. Scattering was found to increase linearly with the pressure of the scattering vapor, to decrease with increasing energy of the incident ions for all ions studied, and to decrease with the mass of the incident ions.

THE classic experiments of Rutherford on the bombarding of gold foil by alpha-particles and his theory of a nuclear atom[1] provided a working hypothesis for the study of the scattering of charged particles by atoms. Since those beginnings, impacts between particles of small mass and gaseous atoms have been studied by others using in their theories mechanisms of electrostatic repulsion, short range attractive forces, and polarization of the particles. These investigations also aimed toward securing a possible explanation of results from classic or wave mechanical laws for a rigid sphere atomic model. Heavier particles, such as positive ions of the alkali metals, also have been used for the study of scattering laws. Scattering at very small angles was investigated by C. A. Frische[2] and A. G. Emslie,[3] angular distribution and energy loss of scattered positive ions by A. G. Rouse.[4] Scattering at a single angle obviates some of the experimental difficulties by simplification of the apparatus and elimination of moving parts. A scattering angle of 90° has several advantages. For, using a suitable set of slits at right angles to the path of the incident ion beam, it is possible to register practically all the ions scattered at this angle; hence the pressure of the scattering gas may be kept lower than would be feasible with a smaller movable collector, or alternatively, at the same gas pressure a greater scattered beam intensity may be obtained. Furthermore, by proper arrangement and control of slits, it is

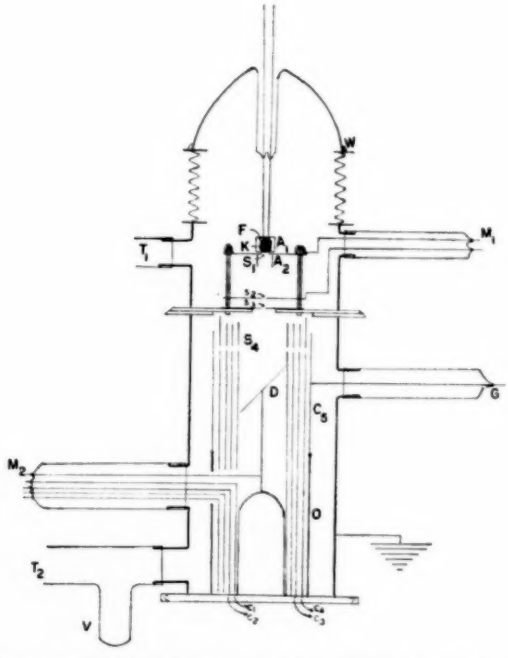

FIG. 1. Positive ion scattering apparatus. F is the filament; K the catalyst; S_1, S_2, and S_3 the collimating slits; A_1 a nickel cylinder surrounding the catalyst; A_2 a nickel collar; T_1, T_2 tubes to gauge and pumps; S_4 slits for path of scattered beam; D the collecting disk; O Pyrex cylinder; M_1, M_2 electrical leads; W Apiezon "W"; V mercury well; C_1, C_2, C_3, C_4 nickel cylinders with slits; C_5 the collecting cylinder; G the lead to grid of amplifier tube. S_1 was made from 1 to 15 volts negative with respect to the filament, while S_3 was made from 3 to 20 volts more negative than S_2. C_2 was kept 2.5 volts negative with respect to ground in order to prevent electrons, produced by ionization, from reaching the collector. It has been found that such electrons have little energy. (Rouse, reference 4, p. 1242.)

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[1] E. Rutherford, J. Chadwick, and C. D. Ellis, *Radiations from Radioactive Substances* (Cambridge University Press, 1930), pp. 191–280.

[2] C. A. Frische, Phys. Rev. **43**, 160–168 (1933).

[3] A. G. Emslie, Phys. Rev. **53**, 680 (1938).

[4] A. G. Rouse, Phys. Rev. **52**, 1238–1244 (1937).

possible to prevent electrons, whether scattered or liberated in the scattering region, from reaching the collector.

Apparatus. Procedure

With these advantages in view, an investigation of the scattering at 90° of positive alkali ions in mercury vapor was carried out for potassium, rubidium, and cesium. The source of ions was a block of Kunsman catalyst,[5] K in Fig. 1, heated by a tungsten filament F and mounted above a set of three circular collimating slits by which the ions were accelerated and directed down along the common axis of five coaxial nickel cylinders where mercury vapor was maintained at a known pressure. The slit S_4, 1/16 in. wide, extended almost the entire distance around the

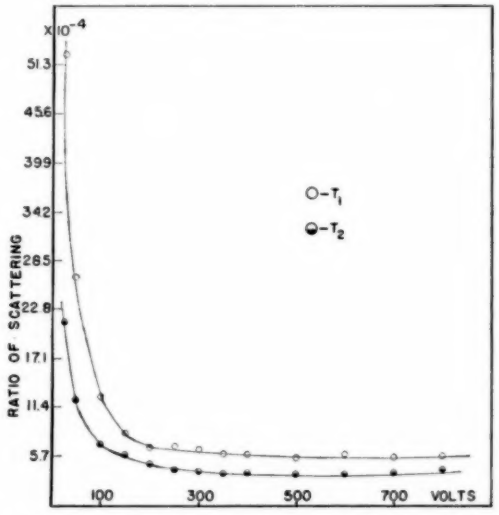

FIG. 2. Scattering of potassium ions. Ordinate is ratio of (current to collector cylinder)/(current to elliptic disk). The unit, 5.7×10^{-4}, is the ratio of the sensitivity of the amplifier to that of the galvanometer. Abscissae represent the total accelerating voltage, i.e., between the filament and the third slit. $T_1=76.5°$ to 77.5°C, $T_2=65°$ to 66°C.

four inner cylinders, C_1, C_2, C_3, C_4, a short distance from the upper end. The outermost cylinder C_5, the collector for the scattered ions, was connected by a well-insulated and well-shielded lead wire to the grid of a D-96475 electrometer tube in a Penick amplifier circuit[6] of sensitivity 5.7×10^{-15} amp./mm. The mercury vapor, the scatterer, was supplied from a well in a

[5] C. H. Kunsman, Science **62**, 269–270 (1925).
[6] D. B. Penick, Rev. Sci. Inst. **6**, 115–120 (1935).

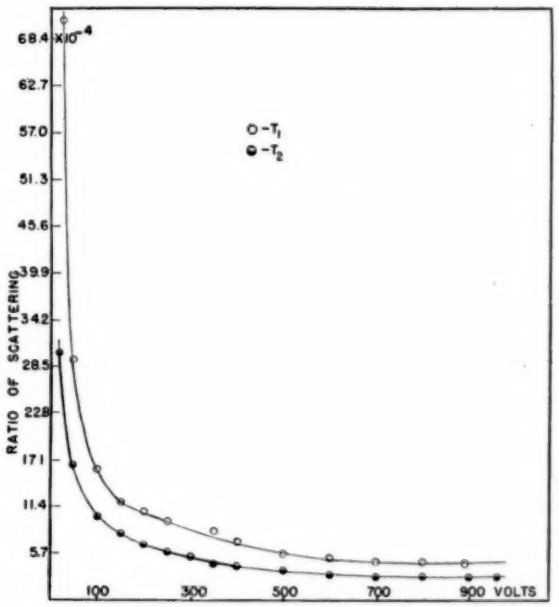

FIG. 3. Scattering of rubidium ions. See Fig. 2 for ordinate and abscissa. $T_1=90.5°$ to 93.5°C, $T_2=78.5°$ to 79.5°C.

side tube connected to the scattering chamber. The temperature of the well was used to measure the mercury vapor pressure within the cylinders where the temperature was maintained at a slightly higher value to prevent excessive condensation of the vapor. D, an elliptic disk placed in the path of the incident beam to collect the incident ions, was set with its normal at an angle of 45° to the beam to decrease the possibility of reflected ions reentering the incident beam, and was connected to a galvanometer of sensitivity 10^{-11} amp./mm. The incident current to D and the scattered current to the outermost nickel cylinder were measured simultaneously, thus making unimportant any fluctuations in ionic emission. The solid angle subtended by the collecting cylinder was 1/28 of the total solid angle and made possible the collection of practically all the ions scattered at 90°.

Results. Discussion

Figures 2–4 are the results of a study made of the scattering ratio (the scattered current/incident ion current) in relation to increase of the total voltage accelerating the ions. The voltage plotted on the curves is the net accelerating voltage for the incident ions and was measured between the tungsten filament which held the

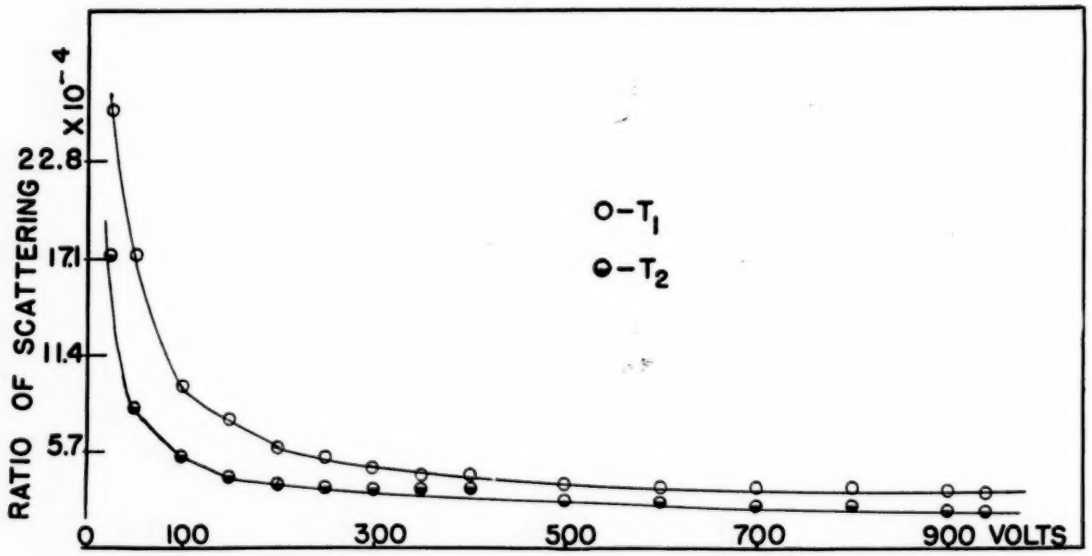

FIG. 4. Scattering of cesium ions. See Fig. 2 for ordinate and abscissa. $T_1 = 80.5°$ to 81°C, $T_2 = 60°$ to 62.3°C.

catalyst and the earthed third slit. The data were repeatable, and averages of several runs for the same range of temperature have been used in these curves. It is noted that 90° scattering always decreased with increase of accelerating voltage for all pressures used. To investigate the possibility of multiple scattering, measurements were made of variation of ratio of scattering with increase of pressure of the scattering mercury vapor. Results (Fig. 5) show that for the three alkali ions studied the scattering ratio increased linearly with the pressure of the scattering vapor, thus giving evidence that no onset of multiple scattering occurred.

The possibility of scattering other than that caused by mercury vapor from the supply well was tested. Evidence for its occurrence was the existence of a considerable current to the collector cylinder when the scattering chamber was heated to 70 or 80°C while the mercury well was kept at room temperature or lower, whereas this was not found when both were at room temperature; but if during a temperature run the chamber temperature was maintained only a few degrees above the mercury well temperature, the ratio of scattering increased linearly with the vapor pressure as mentioned above. To investigate the cause of this condition, pumping was continued for 30 hours with the supply well packed in ice at 0°C and the scattering chamber kept at 90°C or above except for one period of several hours during the night when the temperature was allowed to fall to 70°C. Scattering ratio readings taken at intervals during this test gave results as shown in Fig. 6, where it is seen that, for 100-volt rubidium ions, in 30 hours the ratio fell from 10.5×10^{-4} to 1.88×10^{-4}. This suggests a supply of scattering vapor other than the supply well, probably mercury vapor which could not be removed easily from side tubes, but as a background the residual current was not large enough to cause any serious masking of the scattering results.

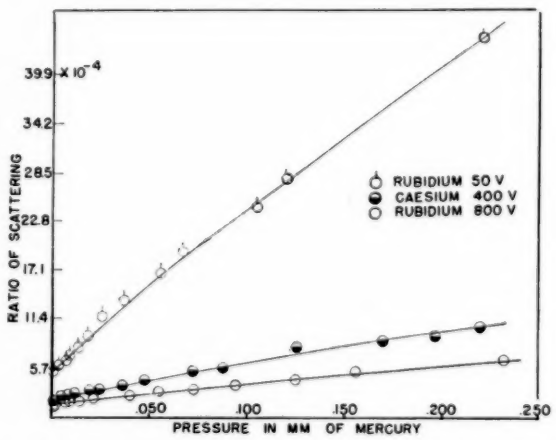

FIG. 5. Representative vapor pressure curves for two types of ions studied. See Fig. 2 for ordinate. Vapor pressure plotted is obtained from temperature as read on a thermometer mounted beside the mercury well in an oil bath surrounded by heating coils.

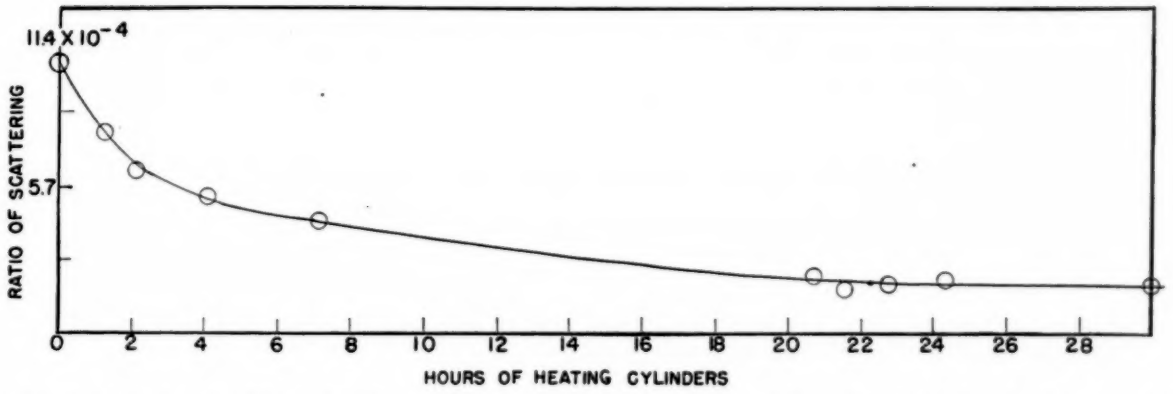

FIG. 6. Scattering of rubidium ions in relation to time of heating. See Fig. 2 for ordinate. During the time recorded on this graph the mercury well was packed in ice while the cylinders were heated to 90°C during the day and 70°C during the night.

Other sources of possible errors in incident current readings may have been caused by: (1) reflection of ions from the walls of the innermost cylinder or from the disk itself; (2) ionization products such as electrons and mercury ions; (3) scattering throughout the length of the beam; and (4) uncertainties in scale readings. The scattered current values would be less likely to be affected by the first two of these sources of error since the slit system would minimize errors due to reflection, the negative potential on the second cylinder retards electrons, and the probability of mercury ions reaching the collector cylinder is small except for those formed beyond the last slit. The probability of scattering from the scattered beam is about equal to that of scattering from the incident beam since the paths are comparable. Uncertainties in readings were chiefly those of the occasionally unstable zero of the galvanometer which was connected to the disk and incomplete knowledge of the extent of temperature equilibrium. The former was of importance only when the incident beam dropped to small values where it may have caused an error as high as 10 percent. The latter did not affect the data for the voltage curves as the temperature varied little during the runs.

CONCLUSION

The present experiments show greater 90° scattering for low energy ions. There is not complete agreement between this result and that of some former investigations of scattering with angle in a different type of apparatus, where it was found that scattering did not always decrease with increasing voltage but in some cases showed an increase,[4] whereas here it decreased for the three ions studied. These results are not entirely compatible with rigid sphere scattering, which does not depend on the kinetic energy of the impinging particle, but lie somewhat between this and Rutherford scattering, and in general suggest the action of other forces, such as polarization of the particles. There is noted also a decrease in scattering with increase of mass of the incident ions.

In conclusion, the author wishes to acknowledge gratefully the guidance and valuable suggestions of Doctor Arthur G. Rouse, under whose direction this work was done; also courtesies extended by the Reverend James I. Shannon, S.J., director of the Department of Physics, Professor A. H. Weber, and other members of the staff and department.

The Values of R and of e/m, from the Spectra of H, D and He^+

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The 1940 data of Drinkwater, Richardson and Williams (DRW) on the H_α and D_α lines have been completely recalculated, to get values of the Rydberg constant for hydrogen and deuterium, and from these, for helium and for infinite mass. Explicit equations, some of which have not previously been published or used, are derived for all the necessary calculations. The value of R_∞ now obtained is appreciably higher than that published by DRW, but it is surprisingly low, compared to the value commonly used for the past decade, which is based on the 1927 work of Houston on H and He^+. His work, as well as later work by Chu, is also completely recalculated, with the use of the latest values of all auxiliary constants. About one-half of the proposed change in the value of R_∞ is due to new values of the index of refraction of air. Recent work on this subject is summarized and put in a form suitable for use by spectroscopists. The data of DRW, as well as that of Houston and Chu, lead also to values of E (atomic weight of the electron) and e/m. The explicit equations needed for such calculations are derived. All recent precision work on e/m is also recalculated. Thus one gets finally twelve different precision values of e/m, obtained by seven distinctly different experimental methods. Although the data are not as consistent as could be desired, there are no really serious discrepancies. If the adopted value of the Faraday were raised by about 30 coulombs, almost complete consistency of the e/m values would be obtained. There is, however, no direct experimental evidence to justify such a change. The recommended values of R, e/m and E are listed at the end of the paper. That for e/m is $(1.7592\pm0.0005)\times10^7$ abs. e.m.u., as contrasted with the value 1.7591 ± 0.0003 recommended three years ago.

INTRODUCTION

THE simplest known type of atom is one that consists of a nucleus and a single external electron. Examples of this type are neutral hydrogen, neutral deuterium, and singly ionized helium. Since such an atom represents a two-body problem, it is possible to obtain a complete solution for the frequencies of the resulting spectrum. The solution involves the important constants R_∞ (the Rydberg constant for infinite mass), α (the fine-structure constant) and E (the atomic weight of an electron). Hence, from sufficiently precise and detailed frequency measurements in the spectrum of H, D and He^+, one can evaluate these three constants.

To obtain a value of α, certain measurements in *any one* of the three spectra are sufficient, whereas to obtain R_∞ and E, measurements in any *two* spectra are required. In this latter case the only auxiliary constants needed are the two relevant isotopic masses (in atomic weight units). If, in addition, one assumes a value of the Faraday F, the value of e/m for an electron may be calculated. Furthermore, in the case of the spectra of H and D, only certain small frequency *differences* are needed to evaluate E or e/m; but in order to obtain R_∞, the actual frequencies must be measured. On the other hand, when He^+ is one of the two spectra used, the actual frequencies must be known to obtain E, (and e/m), as well as to obtain R_∞. Finally, it should be noted that it is a wave-length *in air* that is ordinarily measured, and hence the value of the corresponding index of refraction of air is another necessary auxiliary constant. In fact the results of recent work on the index of refraction of air are chiefly responsible for the appreciable change now recommended for the hitherto accepted value of the Rydberg constant.

The primary purpose of the present paper is to consider in some detail the numerical values of R_∞ and e/m given by recent experimental work in this field, as recalculated with a consistent set of auxiliary constants, and as directly as possible from the original data. The calculation of α involves so many additional considerations, and so much additional experimental data, that a separate paper is needed for any adequate presentation. Such discussion of α as occurs in the present paper is therefore purely incidental to the calculation of R and of e/m.

In the course of these calculations I have come across several small but not negligible errors, some in the theory and others purely arithmetic. Furthermore, the method of calculation employed in the literature has often not been as direct as possible. A second purpose of the paper

is therefore to present explicit equations, in what appears to be the most convenient form, for the several desired quantities in terms of the experimentally determined quantities. Many of these equations, so far as I know, have not previously been published or employed. Aside from their convenience for calculation, such explicit equations are needed in order to determine correctly, by propagation of errors, the probable error of the final result, as a function of the probable errors assigned to the various directly measured quantities.

The original purpose of this work was to calculate a new value of R_∞. Such a calculation incidentally results in an evaluation of e/m, and in order to make the paper reasonably complete, I have accordingly examined several additional papers that yield a value of e/m (but *not* of R_∞), from measurements in the spectra of H, D and He^+. The paper concludes with a brief discussion of all precision values of e/m that have been obtained in recent years, and a calculation of the present most reliable value of this important constant.

Theory

In a two-particle atom such as neutral hydrogen, the electron and nucleus each revolve around the common center of mass. If the mass of the nucleus were infinite, the common center of mass would coincide with the center of the nucleus. In this hypothetical case we are concerned with R_∞, the so-called Rydberg constant for infinite mass, for which Bohr derived the theoretical expression $2\pi^2e^4m/h^3c$, where R_∞ is expressed, as usual, as a wave number (cm^{-1} units) and e is in e.s.u. The variation in the value of any actual Rydberg constant, such as R_H or R_D, from that of R_∞ is due solely to the failure of the center of mass of such an atom to coincide with the center of the nucleus.

R_∞ is now given in terms of the three specific Rydberg constants of interest to us by the equations

$$R_\infty = R_H(1+m/m_H), \tag{1}$$

$$R_\infty = R_D(1+m/m_D), \tag{2}$$

$$R_\infty = R_{He}(1+m/m_{He}) \tag{3}$$

where m = mass of electron, m_H = mass of hydrogen *nucleus*, etc. Since only a ratio of masses is involved, we may choose any desired unit of mass. For convenience we accordingly express mass in atomic weight units, on the *physical* scale, and Eqs. (1)–(3) then become

$$R_\infty = R_H(1+E/H^+), \tag{1'}$$

$$R_\infty = R_D(1+E/D^+), \tag{2'}$$

$$R_\infty = R_{He}(1+E/He^{++}) \tag{3'}$$

where E = atomic weight of electron, $H^+ = H-E$, $D^+ = D-E$, and $He^{++} = He-2E$, all on the physical scale of atomic weights.

Any *two* of these last three equations are sufficient, in order to evaluate E and R_∞. Furthermore, knowing E and R_∞ from any two equations, we can use the third equation to evaluate its own specific Rydberg constant. We can also express this third Rydberg constant explicitly in terms of the other two specific Rydberg constants. Such equations are given in this paper.

We first present various explicit equations for E. Since we have

$$e/m = F/E, \tag{4}$$

where F = Faraday, each explicit equation for E has a corresponding explicit equation for e/m. The unit of e/m depends on the system of units in which F is expressed, and we shall use e.m.u., since e/m is customarily given in such units.

From Eqs. (1′) and (2′)

$$E = \frac{H^+D^+(R_D - R_H)}{D^+R_H - H^+R_D}. \tag{5}$$

Similarly, from Eqs. (1′) and (3′)

$$E = \frac{H^+He^{++}(R_{He} - R_H)}{He^{++}R_H - H^+R_{He}}. \tag{6}$$

Now the actual *measured* wave numbers (s), after proper correction to give the "Balmer line" wave numbers, are directly related to R. Thus for the H_α and the D_α lines,

$$s_H = (5/36)R_H, \quad s_D = (5/36)R_D. \tag{7}$$

Therefore, putting Eq. (7) in Eq. (5), we get

$$E = \frac{H^+D^+(s_D - s_H)}{D^+s_H - H^+s_D}. \tag{8}$$

This last equation has been used by R. C. Williams[1] in his evaluation of E and e/m. A similar equation for He^+ and H is not of interest, since "corresponding" lines of He^+ and H have not been precisely measured or, as a more direct statement, the lines of He^+ and H that have been measured precisely are connected with their Rydberg constants by *different* proportionality factors. Hence Eq. (6) must be used, in evaluating E.

Equations (5), (6) and (8) are not in the most convenient form for calculation, nor for showing clearly how the assumed errors in the experimental quantities affect the resulting error in E. To get more convenient equations, we combine Eqs. (1′) and (2′) in a way that employs the familiar relations, if $A/B=C/D$, then

$$\frac{A-B}{B}=\frac{C-D}{D}, \quad \text{or} \quad \frac{A-B}{A}=\frac{C-D}{C}. \tag{9}$$

We thus get, from Eqs. (1′) and (2′), in place of Eq. (5),

$$E=\frac{H^+D(R_D-R_H)}{R_H(D-H)} \tag{10}$$

or, using Eq. (7), we get

$$E=\frac{H^+D(s_D-s_H)}{s_H(D-H)}. \tag{11}$$

The *proportional* errors in D, H, D−H, and s_H are much smaller than the error in the very small difference s_D-s_H. Thus Eq. (11) shows that, to a close approximation, the proportional error in E equals merely the proportional error in s_D-s_H. This equation also shows that, for the purpose of calculating E, it is not necessary to make a precise measurement of s_D and of s_H. Any approximate value from the literature may be used, and the entire experiment consists in measuring, as precisely as possible, the small *difference* s_D-s_H. The same statement applies to e/m, whose value follows from that of E, by merely assuming a value of F in Eq. (4). Thus, putting Eq. (4) in Eqs. (10) and (11) we obtain

$$e/m=\frac{R_H F(D-H)}{H^+D(R_D-R_H)} \tag{12}$$

and

$$e/m=\frac{s_H F(D-H)}{H^+D(s_D-s_H)}. \tag{13}$$

By combining Eqs. (1′) and (3′), using the relations of Eq. (9), we get, in place of Eq. (6),

$$E=\frac{H^+He^+(R_{He}-R_H)}{R_H(He^+-H)}. \tag{14}$$

The corresponding equation for e/m is

$$e/m=\frac{R_H F(He^+-H)}{H^+He^+(R_{He}-R_H)}. \tag{15}$$

This last equation is Eq. (8), p. 46 of G.C.1929,[2] while Eq. (14) is Eq. (7) of the same page. In that paper the value of e/m was calculated from Houston's data[3] on H and He^+. In Eq. (15), the probable error in e/m is due almost entirely to the probable errors assigned to F and to the *small* difference, $R_{He}-R_H$. The errors in R_H, He^+, H^+ and He^+-H are comparatively negligible. It should also be noted that in the case of $H^+=H-E$, $He^+=He-E$, etc., only an approximate value of E need be used. The precise value of E is then given by Eq. (14) or Eq. (11), etc.

Just as Eqs. (1′) and (2′), or (1′) and (3′), have been solved simultaneously for E, so they can be solved for R_∞. But in the literature it has been standard practice to get R_∞ from Eq. (1′), with a value of E obtained by *assuming* values of F and e/m, in Eq. (4), i.e.,

$$R_\infty=R_H\left(1+\frac{F}{(e/m)H^+}\right). \tag{16}$$

I used Eq. (16) on p. 49 of G.C.1929, but one does not thus get the most reliable value of R_∞, since the measurements on He^+ (or on D) are thereby ignored—unless one adopts just the value of E yielded by the experiment. The following equations for R_∞, which give its value directly in terms of the experimental quantities, have not, so far as I know, previously appeared in the literature.

[1] R. C. Williams, Phys. Rev. **54**, 568 (1938).

[2] R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929). This paper is always referred to as G.C.1929.

[3] W. V. Houston, Phys. Rev. **30**, 608 (1927).

From Eqs. (1′) and (2′), by eliminating E, we get

$$R_\infty=\frac{R_H R_D(D-H)}{D^+R_H-H^+R_D}. \tag{17}$$

This equation corresponds to Eq. (5) for E, and again by using Eq. (7) we get

$$R_\infty=\frac{36}{5}\left\{\frac{s_H s_D(D-H)}{D^+s_H-H^+s_D}\right\} \tag{18}$$

which corresponds to Eq. (8) for E. Just as in the case of Eqs. (5) and (8), we can get a more convenient form of Eqs. (17) and (18) by using the relations of Eq. (9). Thus from Eqs. (1′) and (2′) we get

$$R_\infty-R_H=\frac{R_D-R_H}{1-(R_DH^+/R_HD^+)}. \tag{19}$$

In order to evaluate R_∞ we therefore need to calculate accurately only the *small* difference $R_\infty-R_H$, instead of the large factors of Eq. (17).

In terms of wave numbers Eq. (19) becomes

$$R_\infty=\frac{36}{5}\left\{s_H+\frac{s_D-s_H}{1-(s_DH^+/s_HD^+)}\right\}. \tag{20}$$

Equations (19) and (20) thus represent more convenient forms, for accurate calculation, of Eqs. (17) and (18), and in fact Eqs. (19) and (20), when multiplied out, go directly into Eqs. (17) and (18).

In a similar way, from Eqs. (1′) and (3′), we get

$$R_\infty-R_H=\frac{R_{He}-R_H}{1-(R_{He}H^+/R_HHe^{++})}, \tag{21}$$

which corresponds to Eq. (19).

One can, of course, get from Eqs. (1′) and (3′) the less convenient form, corresponding to Eq. (17). It is

$$R_\infty=\frac{R_H R_{He}(He^+-H)}{He^{++}R_H-H^+R_{He}}. \tag{22}$$

This completes the equations for evaluating R_∞. But, as already noted, one can also express any one of the three Rydberg constants explicitly in terms of the other two. We shall give the result only for R_{He} in terms of R_H and R_D, and then only in the form that uses the relations of Eq. (9). This result is

$$R_{He}-R_H=\frac{D(R_D-R_H)(He^+-H)}{He^+(D-H)} \tag{23}$$

or, in terms of wave numbers,

$$R_{He}=\frac{36}{5}\left\{s_H+\frac{s_D-s_H}{\left(\frac{He^+(D-H)}{D(He^+-H)}\right)}\right\}. \tag{24}$$

We have already noted how the error in E depends upon the errors in s_H and s_D. Let us now determine, from Eq. (20), the corresponding error in R_∞. We note in the first place that the denominator, lying under (s_D-s_H) as numerator, has a value close to 0.5, since s_DH^+/s_HD^+ equals approximately 0.5. Hence the assigned probable errors in s_D and s_H, as they occur in this denominator, produce a negligible effect on R_∞, as compared to these same errors, applied to the *small* difference s_D-s_H.

For a similar reason the small probable errors in H^+ and D^+ may be neglected. Thus for the purpose of calculating the probable error of R_∞ one can, to a very close approximation, merely assume that the denominator lying under s_D-s_H, in Eq. (20), is free from error, and has the value 0.5. The equation then becomes

$$R_\infty=\frac{36}{5}\{2s_D-s_H\}. \tag{25}$$

From the assigned errors in s_D and s_H, we now calculate by propagation of errors the resulting error in $2s_D-s_H$, and the *proportional* error in this quantity is seen to equal the proportional error in R_∞.

In particular, if both s_D and s_H are assigned the *same* absolute error e, then the absolute error in $2s_D-s_H$ is $e\sqrt{5}$, and since $s_D\sim s_H$, or $2s_D-s_H\sim s_H$, the *proportional* error in $2s_D-s_H$ (*and* in R_∞) equals $e(5)^{\frac{1}{2}}/s_H$. In other words, the proportional error in R_∞ is, to a close approximation,[4] $\sqrt{5}$

[4] This method of calculating the probable error in R_∞ is essentially equivalent to writing out the rather complex expression for the probable error, as given rigorously by the law of propagation of errors [R. T. Birge, Am. J. Phys. **7**, 351 (1939)] and then neglecting various terms of the expression that are found to be negligibly small compared to the remaining terms. It must be remembered, in this connection, that Eq. (25) is *not* sufficiently accurate for the calculation of a precision value of R_∞.

times the assigned proportional error in s_H (or in s_D).

In a similar way, the denominator of Eq. (24) is very closely $\frac{2}{3}$, and Eq. (24) is therefore approximately

$$R_{He}=\frac{36}{5}(\tfrac{3}{2}s_D-\tfrac{1}{2}s_H) \qquad (26)$$

from which one can quickly calculate the probable error in R_{He}, resulting from the assigned probable errors of s_D and s_H. In particular, if both s_D and s_H have the same assigned error, the proportional error in R_{He} is $(5/2)^{\frac{1}{2}}$ times the proportional error of either, and hence only $(1/2)^{\frac{1}{2}}$ as great as the resulting proportional error in R_∞.

One can obviously express either R_∞ or R_{He} in terms of its divergence from R_D, instead of from R_H. Thus Eq. (19), or its more convenient form, Eq. (20), may be replaced by

$$R_\infty=\frac{36}{5}\left\{s_D+\frac{s_D-s_H}{\dfrac{s_H\cdot D^+}{s_D\cdot H^+}-1}\right\}. \qquad (27)$$

But Eqs. (20) and (27) are merely different forms of the same equation and hence necessarily yield identical values of R_∞, and also identical probable errors.

The calculated values and calculated probable errors given in the following sections of the paper have been obtained by the use of the equations given in this section,—in particular, Eqs. (11), (13), (14), (15), (20), (21), (24), (25), and (26).

Index of Refraction of Air

In G.C.1929 the adopted value of R_∞ was $109{,}737.42\pm0.06$ cm^{-1}. This value, as already stated, was based on Houston's data.[3] With the same data but with more recent values of the auxiliary constants, I obtained,[5] in August 1939, the value $109{,}737.45\pm0.06$ cm^{-1}. Since then there has appeared an important paper by Drinkwater, Richardson and Williams,[6] who obtained $R_\infty=109{,}737.264$ cm^{-1}, with the auxiliary constants of G.C.1939. I have now recalculated their data and obtain $109{,}737.303\pm0.017$ cm^{-1}. The causes of this revision appear in the detailed discussion to follow. It is, however, immediately obvious that the new value of R_∞ deviates by a surprisingly large amount from the 1929 value. In fact most of the rather large probable error of ±0.06 cm^{-1} in the 1929 result arises from the necessary uncertainty of the value of the international meter in terms of the red cadmium wave-length. This wave-length is 6438.4696 I.A., *defining* the I.A. system of wave-lengths, but it is $(6438.4696\pm0.0020)\times10^{-8}$ cm in the c.g.s. system.[7]

The probable error in the 1929 value of R_∞, *in the* I.A. *system*, was believed to be only about 0.02 cm^{-1}, as contrasted with the change of 0.12 cm^{-1} now suggested. One important cause for this large change, as DRW point out, is the new value of the index of refraction of air used by them. I shall therefore, before proceeding further in the calculation of R_∞, summarize the present experimental data on the dispersion of air. Such a

[5] As a preliminary to a new detailed article on the general constants, I compiled, in August 1939, a mimeographed list of constants, together with a brief explanation of the more important changes. This list will be called G.C.1939. As a result of the appearance of new data, as well as of numerous suggestions received since then, many changes have been made in the list. The present article gives the detailed explanation of the change in R_∞.

[6] J. W. Drinkwater, Sir Owen Richardson, and W. E. Williams, Proc. Roy. Soc. **A174**, 164 (1940). To be referred to as DRW.

[7] The ±0.0020 estimate of error is the value that is needed to give Houston's estimate[3] of the absolute error in R_H and R_{He}, as contrasted with the error in their difference, used on p. 46 of G.C.1929. J. E. Sears and H. Barrell, Trans. Roy. Soc. **A233**, 143 (1934) give a list of four values of the wave-length of the red cadmium line, as measured directly in terms of the international standard meter. The unweighted average is $(6438.4696\pm0.0004)\times10^{-8}$ cm. In a later report J. E. Sears, Science Progress **31**, 209 (1936), adds two more recent measurements by Kösters and Lampe, at the Reichsanstalt. The new unweighted average is 6438.4690 (Sears gives 6438.4693, and the origin of his average is not evident), but the probable error is still ±0.0004. L. J. Briggs, Rev. Mod. Phys. **11**, 111 (1939), reproduces Sears' table, but without the original references. In spite of the remarkable agreement shown by the various measurements of the red cadmium line (the *average deviation* from the mean is only one part in seven million), it seems necessary to adopt the larger uncertainty of $\pm0.0020\times10^{-8}$ cm, because of the unsatisfactory character of the defining scratches on the international meter. W. E. Williams, Nature **135**, 496 (1935), gives a photograph of one of the terminal scratches on substandard meter No. 26, magnified 300 diameters. The scratch, which is actually a *series* of rather irregular parallel furrows, is over two mm wide (i.e., 0.006 mm on the actual meter bar, or 6 parts in 10^6 of its length). Thus the adopted probable error in the wave-length of the red cadmium line corresponds to an error of only 1/20 of the width of such a terminal scratch. The fact that the average deviation of the results of different observers corresponds to only 1/40 of the width is chiefly evidence of a uniformity of *interpretation* of the terminal scratches on the international meter bar.

summary seems especially advisable, because thus far no tabulated data have been published in the form needed in spectroscopy.

Since 1918 all measured wave-lengths in spectroscopy have been reduced to vacuum by the use of Meggers and Peters' formula[8] for the dispersion of air. The well-known tables of Kayser[9] are based on their data. But since 1918 the national physical laboratories of Germany, France and England have made new measurements, with almost identical results, but the new results differ considerably from those of Meggers and Peters. The German work[10] has been published only in abstract form, and the paper giving the French work[11] is not readily available. Fortunately, however, all of the results are summarized in the report on the English work[12] although, as just noted, not explicitly in the form needed by spectroscopists.

All standard spectroscopic wave-lengths are based on the wave-length of the red Cd line, in "normal" air, at 15°C, 760 mm. "Normal" air is at present taken to mean air free from water vapor, but containing 0.03 percent of CO_2. Now all of the recent published results on the index of refraction of air refer to CO_2-free air. To reduce them to "normal" air I have added 0.044×10^{-6} to the value of μ, in accordance with the data of Barrell and Sears.[13] Their published equation for the 20°C value of μ for CO_2-free air[14] has been reduced to 15°C by the use of their own measured value of $\alpha=0.003674$. Perard's results[11] have been changed from 0°C to 15°C by means of his measured value of $\alpha=0.003716$. Kösters and Lampe's results[10] have been changed from 20° to 15° by means of their quoted $\alpha=0.00367$. The exact constitution of the air used by Meggers and Peters[8] was not measured, and it is now merely assumed to have been "normal" air, so that no correction for CO_2 content needs to be made.

One further recent investigation on the dispersion of air is that of Bender.[15] His results differ from those of references 10, 11 and 12 even more than do those of Meggers and Peters, and in the opposite sense. His equation for μ at 0°C has been reduced to 15°C by the Barrell and Sears value of the observed α for air (0.003674), in place of the coefficient of a perfect gas (0.003661) used by Bender himself.

Remembering that all published results, except those of Meggers and Peters, refer to CO_2-free air, we then get, finally, for the dispersion of "*normal*" air at 15°C, 760 mm pressure,

$$(\mu-1)\times10^6=a+b/\lambda^2+c/\lambda^4 \qquad (28)$$

where λ is the wave-length in air, in microns, and the coefficients have the following values.

	a	b	c
Reference 8 (M and P)	272.643	1.2288	0.03555
Reference 10 (K and L)	272.742	1.5017	0.01834
Reference 11 (Perard)	272.860	1.4002	0.02994
Reference 12 (B and S)	272.581	1.5453	0.01268
Reference 15 (Bender)	273.531	1.4946	0.03990

One can get a proper comparison of these various results only by noting the resulting values of μ, at various parts of the visible spectrum. Such typical values of $(\mu-1)\times10^6$ are as follows.

Reference	8	10	11	12	15
λ6438.47	275.814	276.471	276.412	276.383	277.369
λ5085.82	277.925	278.822	278.711	278.745	279.906
λ4358.32	280.097	281.156	281.061	281.068	282.505

It will be noted that references 10, 11 and 12 agree almost perfectly, whereas the results of reference 8 are low and those of reference 15 are high. In all of the calculations of this paper I have used the Barrell and Sears' 1939 dispersion curve (reference 12), since their work is the most recent, and appears to be also the most thorough.

In 1934 Sears and Barrell,[7] in connection with their measurement of the red Cd line in terms of the standard meter, made a determination of μ for air, for the red Cd line only. The value that they obtained, for "normal" air, is 276.494.[16] This gives 1.7802A for the wave-length correction of the red Cd line to vacuum. Hence if, in agreement with Sears and Barrell,[7] we adopt 6438.4696×10^{-8} cm as the best value of the wave-length in "normal" air, the best value in

[8] W. F. Meggers and C. G. Peters, Bull. Bur. Stand. **14**, 697 (1918).
[9] H. Kayser, *Tabelle der Schwingungszahlen* (Leipzig, 1925).
[10] Kösters and Lampe, Physik. Zeits. **35**, 223 (1934).
[11] A. Perard, Trav. Bur. int. Poids Mes. **19**, 1 (1934).
[12] H. Barrell and J. E. Sears, Phil. Trans. **238**, 1 (1939).
[13] Reference 12. See p. 54.
[14] Reference 12. See p. 30.
[15] D. Bender, Phys. Rev. **54**, 179 (1938).

[16] Sears and Barrell give μ only for CO_2-free air, but their published values of λ6440.25099 in vacuum and λ6438.4708 in "normal" air correspond to this value of $(\mu-1)\times10^6$, as contrasted with their 1939 value of 276.383, as already given.

vacuum is 6440.2498×10^{-8} cm on the basis of their 1934 work. On the other hand, the 1939 work of Barrell and Sears[12] gives 1.7795A as the correction, and hence 6440.2491×10^{-8} cm as the wave-length in vacuum. This 1939 work evidently appeared just as the DRW paper[6] was ready for the press. Hence all of the published DRW results are based on the 1934 value of λ6440.2498 as the vacuum wave-length, and to these they have added adjusted values corresponding to the 1939 value of λ6440.2491. In discussing their data, it is more convenient to leave it in its original form, and finally to make this small adjustment, just as DRW have done. It amounts to an *increase* of each wave number by 1.687 parts in 10^7. This increase is 0.0016_{56} cm^{-1} for the H_α and D_α lines.

Experimental Data of DRW, and Calculations

In order to obtain a value of R_x, DRW[6] measured *in vacuum* with a reflection echelon the wave-lengths of the H_α and D_α lines. This instrument consisted of 40 plates, each 6.88 mm thick, and had a calculated resolving power of 0.018 cm^{-1}, or of 846,000($=\lambda/\Delta\lambda$) at the wave-length used. The chief objection to this type of instrument is doubtless the limited field (not over two spectral orders) and the consequent radical warping of the true intensity distribution by the "envelope" of the diffraction pattern. However, when the theoretical correction had been made for this warping, the resulting corrected micro-photometer curves were not only extremely self-consistent, but they also satisfied the various known or expected intensity relations. Hence the final experimental results appear to be quite reliable. The wave-lengths in vacuum of the H_α and D_α lines were measured directly in terms of the red Cd line, so that, as already noted, only the vacuum wave-length of that line need be known. DRW publish only the resulting wave numbers in vacuum of the various lines measured.

The theoretical pattern of the fine structure components of the H_α (and D_α) line and the energy level diagram from which the pattern is obtained, are given by DRW on page 165 of their paper. Each of the levels lies *below* the "Balmer" level by an amount,[17]

$$\Delta T=\frac{R\alpha^2Z^4}{n^3}\left(\frac{1}{j+\frac{1}{2}}-\frac{3}{4n}\right) \tag{29}$$

where R_H should be used for H_α and R_D for D_α, with $Z=1$. In the case of He 4686 one uses R_{He} and $Z=2$. The "Balmer" lines are given by the simple formula

$$s=RZ^2\left(\frac{1}{n''^2}-\frac{1}{n'^2}\right). \tag{30}$$

The problem is thus to obtain in some way the wave number of some *one* fine structure component, and then to apply the necessary correction to give the wave number of the Balmer line, which for H_α and D_α corresponds to $n'=3$, $n''=2$. The component chosen by DRW[6] and by Houston[3] is number one, for which $j'=5/2$, $j''=3/2$. This, the strongest of the predicted five components, cannot be resolved from components 4 and 5, which should lie to the long wave-length side at distances of approximately 0.036 and 0.144 cm^{-1}, with theoretical intensities 1/9 and 1/45 of that of component 1. The "center of mass" of these three components accordingly lies 0.00637 cm^{-1} to the red of component 1, if $1/\alpha$ is taken as 137. Houston[3] used a correction of 0.0056 cm^{-1}, and Williams and Gibbs[18] pointed out that, on the foregoing simple assumptions, 0.0063 cm^{-1} should have been used.

The problem is, however, much more involved, since each fine structure component has its own intensity distribution, due mainly to the Doppler effect. The half-width depends on experimental conditions, and must be determined in each case more or less empirically.[19] But both Williams and Gibbs[18] and DRW[6] agree that if the upper part of the intensity curve is used to locate its "center line," component 5 has a negligible influence and this center line lies almost exactly 0.0036 cm^{-1} to the red of component 1. Incidentally this is just

[17] See H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill, 1934), p. 137.

[18] R. C. Williams and R. C. Gibbs, Phys. Rev. **45**, 491 (1934).

[19] Thus R. C. Williams and R. C. Gibbs, Phys. Rev. **45**, 475 (1934) find half-widths of 0.180 cm^{-1} and 0.171 cm^{-1} for the components of H_α and D_α, respectively. Their paper gives a detailed account of the method used by them in analyzing the microphotometer curves. Different investigators have used somewhat different methods.

the correction gotten on the simple "center of mass" theory, when the very weak component 5 is ignored.

In subsequent work R. C. Williams[1] found a half-width of 0.165 cm^{-1} and a correction of 0.0041 cm^{-1} for the effect of component 4 of H_α. He then makes an additional correction of -0.0012 cm^{-1} for the effect of component 3, which consists really of two coincident components, of total intensity about $\frac{1}{8}$ that of component 1, and which lies 0.221 cm^{-1} to the violet of component 1. DRW give only the position of their 1,4 complex and state that the effect of component 3 has already been taken into account in determining the position of this complex. Williams[1] uses slightly different corrections for H_α and D_α whereas DRW use the same correction for both. A general study of the evidence indicates that 0.0036 cm^{-1} is probably the best correction to be applied to the data of both Houston[3] and DRW,[6] and for both the H_α and the D_α lines. As a matter of fact, whether 0.0036 or 0.0056 cm^{-1} is chosen for the correction makes very little difference in the resulting value of the Rydberg constant but, as will be shown presently, Houston's data are internally more consistent when 0.0036 cm^{-1} is used.

Houston also used component 1 of the H_β line to make an additional evaluation of R_H. The simple "center of mass" procedure here gives 0.00269 cm^{-1} as the necessary correction to the 1,4,5 complex. Williams and Gibbs[18] erroneously publish this last result as 0.0029 cm^{-1}, but they find by the type of empirical analysis used for H_α that 0.0024 cm^{-1} is the required correction. This latter figure happens to be just the correction used by Houston,[3] and I have accordingly adopted it.

We now start the explicit calculation of the DRW data on H_α and D_α. The wave number of the 1,4 complex of H_α was obtained from 10 different plates, with an unweighted average of $15{,}233.0654 \pm 0.0003_2$ cm^{-1}, where the stated uncertainty is merely the standard probable error of a mean, and hence is based wholly on internal consistency of the data. To allow for possible systematic errors I have arbitrarily included an additional error of 0.0010 cm^{-1}, which may add to or subtract from the preceding error. Hence the resulting uncertainty (square root of sum of squares of the errors) is $\pm 0.0010_5$ cm^{-1}. DRW base all uncertainties, throughout their paper, on the root-mean-square (r.m.s.) error of a *single* result (or single plate in this case), with no further allowance for errors of any kind. There seems to be no particular logic in such a procedure since according to it a series of observations yields a result no more reliable than a single observation. In this case their published uncertainty is ± 0.0014 cm^{-1}.

We now add 0.0036 cm^{-1} to the wave number just calculated, and thus get 15,233.0690 cm^{-1} for the wave number of component 1. This value is now to be corrected to get the Balmer line. The necessary (negative) correction[20] is, by Eq. (29), $R_H\alpha^2(1/64-1/324)=0.07327$ cm^{-1}, if $1/\alpha=137$. It seems best, wherever possible, to use the value of α determined by the data themselves but, as is well known, it has not been possible to get a very reliable value of α from the analysis of H_α and D_α. On the other hand, the magnitude of the correction is so small in this case that it is almost immaterial what value of α is used. As a matter of fact, these last two facts are connected logically. Thus in the case of λ4686 the correction is large and it is important what value of α is used. But there the fine structure components are more widely spaced and it is possible to get a fairly reliable value of α from their analysis.

With the Balmer line correction just given, we get $15{,}232.9957_3$ cm^{-1} for the Balmer line itself. This result, however, is in terms of the 1934 index of refraction of air.[7] It becomes 15,232.9974 cm^{-1} in terms of the 1939 index,[12] and this last quantity I denote s_H. Thus[21]

$$s_H = 15{,}232.9974 \pm 0.0003_2 \text{ cm}^{-1} \quad \text{or} \quad \pm 0.0010_5 \text{ cm}^{-1}.$$

Multiplying s_H by 7.2 (the reciprocal of $1/4-1/9$ in Eq. (30)) we get

$$R_H = 109{,}677.581_2 \pm 0.002_3 \text{ cm}^{-1} \quad \text{or} \quad \pm 0.007_5 \text{ cm}^{-1}.$$

DRW give $R_H = 109{,}677.583 \pm 0.010$ cm^{-1}.

[20] DRW write 0.072–0.0036 as the total correction to be subtracted, but give this difference as 0.0694, which happens to be nearly correct. (0.0733–0.0036 = 0.0697.)

[21] I give the calculated results of DRW in general with two probable errors. The first is based merely on the internal consistency of the data, whereas the second (which is *adopted*) includes some allowance for systematic error. When only one probable error is stated, it is the latter of the two.

The D_α line is now to be similarly treated, in order to evaluate R_D. The 1,4 complex of this line is measured by DRW on 7 plates, with an unweighted average of $15{,}237.2096 \pm 0.0003_2$ cm^{-1}. The probable error happens to be identical with that for H_α and I have again allowed 0.0010 cm^{-1} for systematic error. As already discussed, a correction of $+0.0036$ cm^{-1} is again to be applied to get component 1, and the correction for the Balmer line is 0.07329 cm^{-1}, the small change from that for H_α being due to the use of R_D in place of R_H. With the additional correction for the 1939 index of refraction, one thus gets finally

$$s_D = 15{,}237.1416 \pm 0.0003_2 \text{ cm}^{-1}$$
$$\text{or} \quad \pm 0.0010_5 \text{ cm}^{-1}$$

and

$$R_D = 109{,}707.419_3 \pm 0.002_3 \text{ cm}^{-1}$$
$$\text{or} \quad \pm 0.007_5 \text{ cm}^{-1}.$$

DRW give $R_D = 109{,}707.421 \pm 0.009_2$ cm^{-1}.

We now calculate R_x directly from the observed values of s_H and s_D, by the use of Eq. (20). For this purpose we need values of the atomic weights of H and D, and for convenience I give at this point all the auxiliary constants that will be needed in the remainder of the work. They are (all on the physical scale)

$H = 1.00813 \pm 0.00001_7$,
$D = 2.01473 \pm 0.00001_9$,
$He = 4.00389 \pm 0.00007$,
$C = 12.01465 \pm 0.00023$,
$F = 9651.4_0 \pm 1.0$ abs. e.m.u.,
$E = 0.0005486$ (used in getting H^+, D^+ etc.),
$p = 1.00048 \pm 0.00002$ (one int. ohm $= p$ abs. ohm),
$q = 0.99986 \pm 0.00002$ (one int. amp. $= q$ abs. amp.),
$pq = 1.00034 \pm 0.00003$ (one int. volt $= pq$ abs. volt),
$c = (2.99776 \pm 0.00004) \times 10^{10}$ cm/sec.

The values of the atomic weights and of p are those used in a previous letter[22] on e/m, but the value of q has been decreased by a significant amount.[23]

Equation (20) then gives

$$R_x = 109{,}737.302_7 \pm 0.005_2 \text{ cm}^{-1}$$
$$\text{or} \quad \pm 0.016_8 \text{ cm}^{-1}.$$

The method of calculating the probable error in R_x, from the assigned probable errors in s_H and s_D, has been discussed earlier in the paper. Equation (20) gives just the result that would be obtained by calculating e/m from Eq. (12), and then using this value of e/m in Eq. (16). This latter procedure was used by DRW, but they obtained $109{,}737.26_4 \pm 0.020$ cm^{-1}, although they used the latest values of the auxiliary constants, as just listed. The discrepancy is due to two errors in their use of Eq. (16). The atomic weight of neutral H was used in place of the correct H^+, and the atomic weight of the mixture of hydrogen isotopes (H and D) was used in place of the correct isotope of mass 1. I noticed the latter error, when the DRW paper first appeared, and calculated corrected values, which DRW later published.[24] Unfortunately I did not notice the

[22] R. T. Birge, Phys. Rev. **54**, 972 (1938).

[23] The values of p and q are now in a very satisfactory state. An entire paper would be required to cover the details, but the values here adopted are obtained as follows. (1) H. L. Curtis, R. W. Curtis, and C. L. Critchfield, J. Research Nat. Bur. Stand. **22**, 485 (1939) obtain $q = 0.99986$ in terms of the N.B.S. int. amp. This becomes 0.999868 in terms of the mean int. amp. (2) P. Vigoureux, N.P.L. Collected Researches **24**, 173 (1938) gets $q = 0.99986$ in terms of the N.P.L. int. amp. which becomes 0.99985 in terms of the mean int. amp. From these two results I get as a final average, $q = 0.99986 \pm 0.00002$, in terms of the mean int. amp. (3) H. L. Curtis, C. Moon, and C. M. Sparks, J. Research Nat. Bur. Stand. **21**, 375 (1938) obtain as the weighted average of this and a previous investigation, $p = 1.000468$ in terms of the N.B.S. int. ohm, or 1.000472 in terms of the mean int. ohm. (4) Two investigations at the N.P.L., one by L. Hartshorn and N. F. Astbury, Phil. Trans. **A236**, 423 (1937), and the other by P. Vigoureux, N.P.L. Collected Researches **24**, 277 (1938) each give $p = 1.00050$ in terms of the N.P.L. int. ohm, or 1.000508 in terms of the mean int. ohm. A slightly higher accuracy is claimed for the N.B.S. work, and I accordingly adopt as a final weighted average, $p = 1.00048 \pm 0.00002$, in terms of the mean int. ohm.

The value of F given in reference 22 is 9651.31 ± 0.80 abs. e.m.u., on the physical scale. A slightly more precise calculation shows that this figure should have been given as 9651.33 e.m.u. The present adopted value is only slightly larger, but actually two large and almost compensating changes have been made. In the first place the value of q has been changed from 0.99993 to 0.99986. This change *decreases* the value of F by 0.67 e.m.u. On the other hand, I have now adopted a certain weighted average of the values of F given by the silver and the iodine voltameters, in place of merely the silver result. This very involved and controversial subject will be discussed in detail elsewhere. The change *increases* the value of F by 0.73 e.m.u. A very small change (from 1.00027 to 1.000272) has also been made in the ratio of the physical and chemical scales of atomic weights. The net result of these various changes is an increase of 0.07 e.m.u. in the value of F.

The atomic weights are the standard values given by M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 245 (1937), except that for carbon, which I have derived from the latest experimental results.

[24] DRW, Proc. Roy. Soc. **A175**, 345 (1940).

other and more serious error until I had started the systematic calculations of this paper.[25]

In addition to R_∞, the data of DRW allow the calculation of E and of e/m. The value of E may be obtained directly from Eq. (11), with the result

$$E=(5.48647\pm0.00059)\times10^{-4}$$
$$\text{or}\quad\pm0.00099.$$

The error in E depends directly on that in (s_D-s_H) and any systematic error in this *difference* is likely to be less than that in either s_D or s_H. Hence the second quoted probable error in E is based on an assumed systematic error of only 0.0006 cm^{-1} in s_D-s_H, in place of the 0.0010 cm^{-1} systematic error already adopted for s_D and s_H, separately.

Then from Eq. (4), or directly from Eq. (12),

$$e/m=(1.75913\pm0.00027)\times10^7 \text{ e.m.u.}$$
$$\text{or}\quad\pm0.00037.$$

DRW, using Eqs. (8) and (4), get $E=(5.48646\pm0.00050)\times10^{-4}$, and $e/m=(1.7591\pm0.0004)\times10^7$ e.m.u. For this last result they used $F=9651.31$ abs. e.m.u.

A discussion of the causes for the deviation of DRW's value of R_∞ from my 1929 value is postponed until Houston's data[3] have been recalculated. But it should be noted at this time that there is a second method for calculating R_∞ from data such as that of DRW. Instead of using Eq. (20), we may use Eq. (1′), or its equivalent, Eq. (16), with some "outside" value of e/m and of F (to give E of Eq. (4)). R_∞ may also be calculated from Eq. (2′), and Eqs. (1′) and (2′) will then yield *different* values of R_∞ unless the adopted value of e/m happens to be identical with the value yielded by Eq. (12). In the case of DRW, the value of e/m given by Eq. (12) does happen to satisfy this condition very closely.[26]

Even in this situation, the resulting probable error in R_∞ will be different, according as Eq. (1′) or (2′) is used, and each error will be different from that resulting from the use of Eq. (20). Furthermore, with equally accurate values of R_D and R_H, the former—used in Eq. (2′)—will lead to the more accurate value of R_∞. This necessary fact is shown clearly by the actual results. With the "outside" values of $e/m=(1.7591\pm0.0005)\times10^7$ and $F=9651.4_0\pm1.0$, and with $R_H=109{,}677.5812\pm0.0075$, we get from Eq. (16)—or from Eqs. (1′) and (4)—

$$R_\infty=109{,}737.303_6\pm0.019_5 \text{ cm}^{-1},$$

whereas with $R_D=109{,}707.4193\pm0.0075$ we get, from Eqs. (2′) and (4),

$$R_\infty=109{,}737.303_2\pm0.011_8 \text{ cm}^{-1}.$$

The value of R_∞ obtained from R_D alone is thus apparently more accurate than that obtained by Eq. (20) from s_H and s_D simultaneously, even though the "outside" value of e/m has been assigned a slightly larger error (±0.0005) than the calculated error (±0.00037) of the "inside" value, and the use of Eq. (2′) involves also the error in F, whereas Eq. (20) does not. It must be realized, however, that the use of Eq. (20), rather than of Eqs. (2′) and (4) with "outside" values of e/m and F, eliminates the possibility of certain types of systematic error (in particular, errors in F), and hence I believe that the result yielded by Eq. (20), i.e.,

$$R_\infty=109{,}737.303\pm0.017 \text{ cm}^{-1},$$

is probably the best to adopt. It is, in fact, the final result, as adopted in this paper, except that the probable error should be increased to ±0.05 cm^{-1} to allow for the uncertainty in the relation of the I.A. to the c.g.s. system of length.

Finally, from DRW's values of R_H and R_D it is possible to calculate any other R, such as R_{He}. This last constant is given by Eq. (24), directly in terms of the original data s_H and s_D, with the result

$$R_{He}=109{,}722.263_5\pm0.012 \text{ cm}^{-1}.$$

[25] This confusion regarding the isotopes of hydrogen is a direct consequence of the unfortunate situation that exists in respect to the symbols in use. In writing equations such as those used in this paper, it is obvious that H and D are more convenient than H^1 and H^2, since double superscripts are thereby avoided. On the other hand, the symbol H represents, to the chemist, the atomic weight of the mixture of hydrogen isotopes H^1 and H^2, just as C represents the mixture of C^{12} and C^{13}. In fact, in setting up a partial table of atomic weights (on the physical and on the chemical scale), as I have done in G.C.1939, it seemed really necessary to use H^1 and H^2. For if H and D are used, how is the atomic weight of the mixture to be symbolized? Thus there are definite objections to each of the two sets of symbols.

[26] The present most probable value of e/m is considered later in this paper.

In addition to the work on R_∞ and e/m, DRW[6] also make a detailed study of the fine structure of H_α and D_α. Such work should lead to a fairly precise value of the fine structure constant. However, as is well known, repeated investigations of this subject have shown rather definitely that the position and intensity of certain components, notably component 3, are not in agreement with theory. Pasternack[27] has tried to explain the observed discrepancies by assuming a displacement of the 2^2S level by about 0.03 cm^{-1}. DRW, however, believe that a slight contamination of the fine structure components of D_α by H_α components, and of both D_α and H_α by molecular lines, is sufficient to account for all observed irregularities. It is just because of such irregularities, which have been known for many years, that so much work has been done on the fine structure of H_α and D_α. There is as yet no reason to suppose that the method we have just used in calculating R_H, R_D, and R_∞ is affected by the observed irregularities, but because of them it has not been possible to get a reliable value of α, as already stated. Furthermore, because of the great amount of experimental work on the subject, a separate article is needed to cover it adequately, as also stated earlier in this paper. Fortunately no similar irregularities have been found in the case of the λ4686 line of He^+, and from this line one can obtain a reasonable value of α, as will be shown presently.

Data of Houston, and Calculations

As already noted, the value of R_∞ given in G.C.1929 was based entirely on Houston's experimental value[3] of R_H, with the use of "outside" values of e/m and F in Eq. (16). Houston's experimental value[3] of R_{He} was not used at all, but it should have been used. It is therefore of interest to calculate the most reliable value of R_∞, by the use of *all* of his data, and with the latest auxiliary constants, and to compare such a revised value with that obtained by DRW. In 1929 I merely accepted Houston's calculated value of R_H, but I will now recalculate it, just as I have done in the case of the DRW work.

Houston calculated R_H from the measured wave-length, *in air*, of component 1 (also called I_a) of H_α and of H_β, and he calculated R_{He} from the measured wave-lengths of components I_a and II_b of the λ4686 line of He^+. The work was done with a Fabry-Perot interferometer, and all wave-lengths were measured against the λ5015 helium line, whose wave-length in air was taken as 5015.6750 I.A. This is also the present accepted wave-length, but the discrepancy that still exists —as will presently be shown—between his value of R_∞ and that of DRW, must be ascribed in the main, according to DRW, to some error in this accepted wave-length.

Houston, in his reduction to vacuum, naturally used the dispersion curve of Meggers and Peters. We shall now use Barrell and Sears[12] 1939 dispersion curve and this change in the dispersion of air alone makes each calculated wave-length in vacuum about 0.004A larger, a by no means negligible change. As already noted, I will use +0.0036 cm^{-1}, in place of Houston's +0.0056 cm^{-1}, for the correction to the 1,4,5 complex of H_α to get the wave number of component 1, but for H_β I retain his correction of +0.0024 cm^{-1}. The only additional quantity needed is the "Balmer" line correction, which for component 1 of H_β is $R_H\alpha^2(1/64-7/3072)=0.0780$ cm^{-1}.

Two further points should be noted. (1) Houston measured the H_α line on 5 plates, and the average wave-length in air of the 1,4,5 complex, as given correctly in his Table I, is 6562.8473 I.A. This wave-length, however, is written and used as 6562.8475 in the calculations of his Table III, thus introducing a very small error. (2) The corresponding complex of H_β was also measured on 5 plates, and the average, as correctly stated in his Table I, and correctly *used* in his Table III, is 4861.3578 I.A. Because of a purely typographical error this wave-length appears in his Table III as 4861.3678 and DRW, overlooking the true situation, point out (reference 6, p. 166) that his stated wave number of H_β in vacuum, in Table III, does not correspond to the stated wave-length in air, on the basis of the Meggers and Peters' dispersion curve.

With these changes I then obtain, by the same process as was used for DRW,

$$s_H = 15{,}233.0113 \text{ cm}^{-1} \text{ from } H_\alpha,$$
$$s_H' = 20{,}564.5643 \text{ cm}^{-1} \text{ from } H_\beta,$$

where s_H and s_H' denote the "Balmer" lines.

[27] S. Pasternack, Phys. Rev. **54**, 1113 (1938).

Multiplication of s_H by 7.2 and of s_H' by 16/3 gives R_H, and the results are

$$R_H = 109{,}677.6813 \text{ cm}^{-1} \text{ from } H_\alpha$$
$$= 109{,}677.6762 \text{ cm}^{-1} \text{ from } H_\beta.$$

The close agreement of these two values is a really remarkable verification of the entire theory of the hydrogen atom. The discrepancy is only $+0.0051$ cm^{-1} (5 parts in 10^8), as contrasted with a *negative* discrepancy of 0.021 cm^{-1} resulting from Houston's own calculated values of 109,677.754 and 109,677.775. With his own correction of $+0.0056$ cm^{-1} in the case of H_α, and with Meggers and Peters' dispersion curve, I obtain 109,677.755 from H_α and 109,677.771 from H_β (discrepancy -0.016 cm^{-1}) as the values of R_H that Houston should have gotten from his data. If now the correction is changed to $+0.0036$ cm^{-1}, the discrepancy is *increased* in magnitude from -0.016 to -0.030 cm^{-1}. With the 1939 dispersion curve, however, the corresponding discrepancies are $+0.0195$ cm^{-1} and $+0.0051$ cm^{-1}. Thus the use of the $+0.0036$ cm^{-1} correction decreases the discrepancy between the values of R_H from H_α and H_β *only* when the 1939 dispersion curve is used. With Meggers and Peters' curve the discrepancy (now of opposite sign) is *increased*. Our final conclusion is, then, that in order to get a consistent value of R_H from Houston's data on H_α and H_β, it is necessary to use the new 1939 dispersion curve and *also* the new $+0.0036$ cm^{-1} correction. This fact may be considered as internal evidence in favor of the use of both.

Houston gives relative weights of 3 to 1 to the two values of R_H from H_α and H_β, and with this weighting I get the weighted average

$$R_H = 109{,}677.6800 \text{ cm}^{-1},$$

which is 0.079 cm^{-1} smaller than his published average, but 0.099 cm^{-1} *larger* than the DRW result. If now we use the Meggers and Peters' dispersion curve, but leave everything else unchanged, the weighted average rises to

$$R_H = 109{,}677.7493 \text{ cm}^{-1},$$

which is 0.168 cm^{-1} larger than the DRW result. The use of Houston's $+0.0056$ cm^{-1} correction raises this figure by only 0.0098 cm^{-1}, and increases the 0.168 cm^{-1} discrepancy by a like amount to 0.178 cm^{-1}. Thus the use of the newer values for the dispersion curve of air decreases the discrepancy between Houston's and DRW's values of R_H only from 0.168 to 0.099 cm^{-1}, and the other changes that have been made in Houston's calculations are considerably smaller.

The final unexplained discrepancy between the results of DRW and Houston may be stated more clearly as follows. Houston measured 6562.8473 I.A. as the wave-length in air of the 1,4 complex of H_α. DRW's published wave number in vacuum, when reduced to wave-length in air by the 1939 dispersion curve, is 6562.8533 I.A.—just 0.006A larger. This difference is many times the apparent probable error of the measurement but, as already noted, Houston's result is based on the λ5015 helium line, whereas the DRW result is based on the λ6438 cadmium line.

This completes the discussion of Houston's value of R_H, and we now consider his value of R_{He}, which is based on the measured wave-lengths of components I_a and II_b of the λ4686 line. For this line $R = R_{He}$, $Z = 2$, $n' = 4$ and $n'' = 3$, in Eqs. (29) and (30). For the I_a component, $j' = 7/2$, $j'' = 5/2$. For the II_b component $j' = 5/2$, $j'' = 3/2$. These are the two strongest components, out of a total of 8 predicted components, and are of nearly equal intensity. Chu[28] gives a diagram of the fine-structure pattern. Because of the great intensity of the two components used, as compared to the remaining components, Houston[3] used merely the observed wave-lengths, without any additional correction (but see footnote 30). Chu[28] later made a more detailed analysis of the microphotometric curves. His results will be discussed presently.

Houston obtained component I_a on 7 different plates, with an average wave-length in air of 4685.8030 I.A., and a mean deviation of 0.0026 I.A. The II_b component was measured also on 7 plates, with an average of 4685.7030 I.A., and mean deviation 0.0012 I.A. In this case we can use the difference of these two wave-lengths to obtain an *experimental* value of the fine structure constant α. With the usual dispersion curve,[12] one obtains for the wave number difference, in vacuum, $\Delta s = 0.45533$ cm^{-1}. This should equal $(101/1296) R_{He} \alpha^2$, thus giving $1/\alpha = 137.038$,

[28] D. Y. Chu, Phys. Rev. **55**, 175 (1939).

which all recent experimental evidence indicates is close to the true value. With this value of α, the negative correction of the I_a component to give the "Balmer" line is $16R_{He}\alpha^2(1/324-1/1024)=0.19723$ cm^{-1}. The negative correction for the II_b component is $16R_{He}\alpha^2(1/108-7/3072)=0.65256$ cm^{-1}. When one thus uses the value of α derived from the data, the two resulting values of the "Balmer" line are necessarily identical, and the result is

$$s_{He}=21{,}324.89082 \text{ cm}^{-1}.$$

Multiplying by 36/7 (the reciprocal of $4(1/9-1/16)$ in Eq. (30)), we get $R_{He}=109{,}722.295_7$ cm^{-1}, which is 0.0322 cm^{-1} larger than the value already calculated indirectly from DRW's data. The agreement is, accidentally, much better than that between the two *directly* calculated values of R_H, by Houston and by DRW. Houston himself, using the Meggers and Peters' dispersion curve and an "outside" value of α, got from the two components slightly different values of R_{He} and a weighted average value[29] of $109{,}722.403\pm0.004$ cm^{-1}.

From Houston's values of $R_H=109{,}677.6800$ and $R_{He}=109{,}722.2957$, as just recalculated, we can now obtain E and e/m by means of Eqs. (14) and (15). The results are $E=5.47829\times10^{-4}$ and $e/m=1.7617_6\times10^7$ e.m.u. No probable error is calculated for this value of e/m, since it is not used in the final average, as discussed later. If Houston's H_α correction of 0.0056 cm^{-1} were used, we would get 1.7621_8. In G.C.1929 (p. 47) I got, from the same data, $e/m=1.7608\pm0.0008$. In 1938 I obtained[22] $1.7601_5\pm0.0008$. These changes indicate very well the effect of varying values of auxiliary constants, and varying methods of reduction of the same data.

We can also obtain R_∞, by means of Eq. (21). The result is $R_\infty=109{,}737.3125$ cm^{-1}, which is only 0.010 cm^{-1} above the adopted DRW result. Houston[3] himself gives $R_\infty=109{,}737.424$ cm^{-1} and this value was *adopted* in G.C.1929 (p. 49). In the case of DRW we have calculated R_∞ also from R_H and from R_D separately, using Eqs. (1′) and (2′) and outside values of e/m and F to get E from Eq. (4). The result from R_D is the more accurate. In a similar way, we can get R_∞ from Houston's value of R_H and from his value of R_{He}, by the use of Eqs. (1′) and (3′). These two new values are 109,737.4024 cm^{-1} and 109,737.3351 cm^{-1}, respectively. Both of these values are higher than that obtained from Eq. (21), and differ considerably from the DRW result. This shows that the previous close coincidence in the values of R_∞ from the DRW and the Houston work is purely accidental, and is due to the fact that real discrepancies in the values of R_H and e/m (or E) happen nearly to cancel each other, in the calculation of R_∞.

Data of Chu, and Calculations

Chu,[28] as already noted, has analyzed the fine structure of He λ4686 and has calculated a value of R_{He}. His work was done under the direction of Houston, with similar apparatus to that used by Houston. The wave-length measurements of both men are based on the λ5015 helium line. Hence it seems legitimate to combine Chu's value of R_{He} with Houston's value of R_H, to get a value of R_∞, and also of e/m.

In Houston's work the two strong maxima of the intensity curve of λ4686 were identified with components I_a and II_b. In Chu's work a careful analysis of the intensity curve was carried out, in much the same way as was done by Williams and Gibbs[19] for H_α and D_α. In the case of λ4686, the fine structure extends over so large an interval, 2.43 cm^{-1}, that with the usual orders of interference of the Fabry-Perot interferometer, there is a great deal of overlapping of orders. By varying the order of interference, the resulting intensity pattern can be made to vary markedly. The corrections necessary to apply to the two strong maxima were calculated by Chu, from his analysis of the intensity curves, for each order of interference used, and these corrections, as might be expected, also varied greatly. In fact, for the II_b component the corrections varied from +0.0012A to −0.0029A. This variation is really an advantage, for if the final corrected wave-length is constant from plate to plate, it is very good evidence that the procedure employed is funda-

[29] Each of Houston's stated errors appears to be based on external consistency, but since only two values are available in each case, internal consistency would yield a far more reliable estimate. I have not carried through a calculation of probable error such as I did in the case of the DRW results, because I am adopting the DRW results. The sole purpose of the present calculation is to get a correct comparison with the DRW results, by the use of the same auxiliary constants and the same method of calculation in each case.

mentally sound. This result was actually attained. Thus the resulting wave-lengths[30] of the II_b component, on the four plates used, varied only by 0.0009A. It was more difficult to measure the I_a component and on one plate (No. 126) its wave-length differs by 0.0037A from the average of the remaining three plates. Chu states that the position of the maximum on the microphotometric tracing of this plate was particularly uncertain.

We shall first follow Chu in accepting the results of all four plates, and we shall also use his assigned weights, which run from 4 to 1. Then for the I_a component the average wave-length in air is 4685.8012A, giving $s=21{,}335.09626$ cm^{-1} for the wave number in vacuum (with the 1939 dispersion curve of air). For the II_b component the corresponding results are 4685.7017A and 21,335.54931 cm^{-1}. These wave-lengths are respectively 0.0018A and 0.0013A larger than Houston's values. The wave number difference is, from Chu's data, 0.45305 cm^{-1}, from which we get $1/\alpha=137.383$. As we have seen, Houston's corresponding result is $1/\alpha=137.038$. Chu does not give explicitly his value of $1/\alpha$ (137.383), but I had calculated it and until the recent work of Christy and Keller[31] I had considered it the best experimental determination, with an assigned probable error of ± 0.4. It is to this value by Chu that I had reference in my own recent letter[32] on the subject.

With Chu's value of α, the "Balmer" corrections for the I_a and II_b components are now 0.19625 cm^{-1} and 0.64930 cm^{-1}, respectively. The necessarily identical value of the Balmer line, from either component, is $s_{He}=21{,}334.90001$ cm^{-1}, and from this we get

$$R_{He}=109{,}722.342_9 \text{ cm}^{-1},$$

which is 0.047 cm^{-1} larger than Houston's value, and 0.079 cm^{-1} larger than DRW's indirect value. Chu himself gives $109{,}722.43\pm 0.04$ cm^{-1}, using Meggers and Peters' dispersion curve.

We can now combine Houston's value of $R_H=109{,}677.6800$ cm^{-1} and Chu's value of $R_{He}=109{,}722.3429$ cm^{-1}, to get, from Eqs. (14), (15), and (21)

$$E=5.484086\times 10^{-4},$$
$$e/m=1.7598_9\times 10^{7} \text{ e.m.u.},$$
$$R_\infty=109{,}737.3756 \text{ cm}^{-1}.$$

It has just been noted that component I_a was observed to be very ill-defined on one of Chu's plates (No. 126), and the results given by this plate are in definite disagreement with those of the remaining three plates. The disagreement is shown clearly by calculating $1/\alpha$ from each plate separately. The results are

Plate	$1/\alpha$
118	137.314
124	136.971
126	139.790
134	136.971

The weighted average value, omitting No. 126, is 137.079 and if I had noticed these facts earlier, I would certainly not have taken Chu's weighted average of all four plates (137.38) as the best experimental value of $1/\alpha$. This seems to be a situation where it is clearly justifiable to discard one plate, and hence it would appear that Chu's best value of $1/\alpha$ is more nearly 137.1 ± 0.2, as compared to the value 136.95 ± 0.05 obtained from x-ray data.[31, 32] Although Houston's value (137.04) is also very satisfactory, it is presumably not as reliable as Chu's, because of Houston's less detailed analysis of his intensity curves.

With plate No. 126 omitted, and with $1/\alpha=137.079$, one gets, from Chu's remaining three plates

$$R_{He}=109{,}722.3280 \text{ cm}^{-1},$$

which is only 0.0156 cm^{-1} larger than Houston's value. Combining this last result with Houston's R_H, we obtain

$$E=5.48225\times 10^{-4},$$
$$e/m=1.7604_8\times 10^{7} \text{ e.m.u.},$$
$$R_\infty=109{,}737.3556 \text{ cm}^{-1}.$$

These results are, I believe, the most reliable that can be obtained from the combined work of Houston and Chu. Their work and the work of DRW furnish all of the experimental data from which one can obtain a precision value of R_∞. In

[30] It is only fair to remark that Houston[2] also recognized clearly the need for making corrections on each individual plate, to get the true positions of the I_a and II_b components. He tried, however, to vary the order of interference in such a way that the various resulting corrections would, *on the average*, be expected to cancel out.

[31] R. F. Christy and J. M. Keller, Phys. Rev. **58**, 658 (1940).

[32] R. T. Birge, Phys. Rev. **58**, 658 (1940).

adopting a final value of R_x one should really consider some weighted average of the two results. But because of the character of the discrepancies, as already discussed, such an average appears to have little meaning. For this reason, and for this reason alone, I have adopted as the final value of R_x merely the DRW result.[33]

On the other hand, the value of e/m just given is to be combined with many other values, later in this paper, to get a final best value. Hence it is necessary to adopt a probable error for it. This value of e/m has been calculated from Eq. (15), and the only probable errors that need be considered are those in F and in the difference $R_{He}-R_H$. The adopted value of F is $9651.4_0\pm1.0$ abs. e.m.u., as already stated.

Houston's two values of R_H (from H_α and H_β) differ by only 0.0051 cm^{-1}, and hence 0.010 cm^{-1} seems a liberal estimate for the probable error of the weighted average (109,677.6800 cm^{-1}). Chu's value of R_{He}, from 3 plates, differs from that calculated from all 4 plates by 0.015 cm^{-1}. Since the omitted plate is obviously poor, 0.010 cm^{-1} again seems a liberal estimate for the probable error of the 3-plate result (109,722.3280 cm^{-1}). Now *both* Houston and Chu base all their wave-lengths on He λ5015. Hence the most serious sources of possible *systematic* error do not appear in the *difference* $R_{He}-R_H$. We therefore get $R_{He}-R_H=44.648_0\pm0.014$ cm^{-1}, and finally

$$e/m=(1.7604_8\pm0.0005_8)\times10^7 \text{ abs. e.m.u.}$$

as the adopted result from the Houston-Chu work.

[33] Professor Houston has called my attention to the fact that the relations between R_H, R_D, R_{He} and R_∞, as obtained by various observers, can conveniently be shown on a graph of the same general character as the Birge-Bond diagram. Thus in Eqs. (1′)–(3′), if we use an *assumed* value of $E(=E_0)$, each experimental value of R_x will yield an *apparent* value of $R_\infty(=R_\infty')$. If now these values of R_∞' are plotted against the reciprocal of the nuclear atomic weight (i.e., against $1/H^+$, $1/D^+$ etc.) as abscissa, all discrepancies are immediately obvious. If there are no discrepancies, all of the points will lie on one straight line. The extrapolation to zero abscissa of the straight line through any two points gives the value of R_∞ resulting from the use of these two data. On such a diagram, the DRW data give one straight line, and Houston's data give another line with a quite different slope, corresponding to the quite different value of e/m yielded by his data. The Houston-Chu data give a line of intermediate slope. The diagram shows immediately that no compromise line will give a satisfactory representation of the data of any one of the different observers.

Experimental Values of e/m from Fine Structure Analysis

a. Work of R. C. Williams

Although we have now covered the experimental data leading to values of R_x, and incidentally of e/m, there are further similar investigations from which one can obtain experimental values of e/m but not of R_∞. I have not examined this additional work with the thoroughness of the preceding, and the following discussion is rather brief.

One important additional investigation on the fine structure of H_α and D_α is that of R. C. Williams, which was carried out under the direction of R. C. Gibbs. In addition to the papers giving the final results on e/m (reference 1) and on α,[34] and the papers already quoted,[18,19] there are other earlier reports.[35–37]

In order to calculate e/m, the *difference* of wave-length of component 1 of H_α and D_α was measured with an interferometer of over 250,000 resolving power (3-mm etalon silvered to reflect over 90 percent). The method of analyzing the fine structure is discussed in references 34 and 19. Williams' published average "peak-to-peak" interval in air for the H_α and D_α lines is 4.14716 ± 0.0004 cm^{-1}. Division by the index of refraction of air (1.00027624) gives 4.146014 cm^{-1} for the interval in vacuum. The use of Meggers and Peters' $\mu=1.0002757$ changes this result only to 4.146017, but Williams gives 4.14610 cm^{-1} as his value in vacuum.

Full details of the corrections to be applied to each complex "peak" to get the position of component 1 are given by Williams in his Table III of reference 1. He finds a *differential* correction of +0.0009 cm^{-1}, but most of this correction is due to a differential correction of +0.0012 cm^{-1} for the effect of component 3. As noted earlier, DRW make no differential correction to their $H_\alpha-D_\alpha$ interval, but their printed results include the correction for component 3. Hence there is no real disagreement between Williams and DRW.

Williams' corrected interval is thus 4.14691_4

[34] R. C. Williams, Phys. Rev. **54**, 558 (1938).
[35] R. C. Gibbs and R. C. Williams, Phys. Rev. **44**, 1029 (1933).
[36] R. C. Williams and R. C. Gibbs, Phys. Rev. **48**, 971 (1935).
[37] R. C. Williams and R. C. Gibbs, Phys. Rev. **49**, 416 (1936), (two abstracts).

cm^{-1} and Eq. (11) then gives E. For convenience in comparing the results of different observers, Eq. (11) may be written as

$$E=(1.3238985\times10^{-4})(s_D-s_H) \qquad (11')$$

with the DRW value of s_H (15,232.9974 cm^{-1}) and the atomic weights already listed. Therefore $E=5.49009_3\times10^{-4}$ from Williams' data. Then from Eq. (4), $e/m=1.7579_7\times10^7$ e.m.u. Williams gives $(5.4902\pm0.0005)\times10^{-4}$ and $(1.7579\pm0.0004)\times10^7$.

In the case of DRW we have already found the result $e/m=(1.75913\pm0.00037)\times10^7$, where the probable error was calculated with some care, and includes a certain allowance for systematic error. In order to get a final weighted average value of e/m, it is necessary to assign *relative* weights to the various results. Hence it is only the *relative* probable errors that are important, and in the case of all the remaining results, we ask ourselves, "If 0.00037×10^7 is taken as a fair estimate of the probable error of the DRW value of e/m, what is a proper estimate for the new investigation, when one considers the relative accuracy of the instruments used, the detailed measurements made, etc.?" The probable errors adopted here are therefore frankly purely personal estimates.

For the R. C. Williams result I *adopt*

$$e/m=(1.7579_7\pm0.0005)\times10^7.$$

b. Work of C. F. Robinson

Robinson has as yet published only an abstract[38] of his investigation, which is a continuation of work started by Houston[39] on an analysis of the fine structure of H_α and D_α by a new method. I am, however, indebted to Professor Houston for further details. Robinson's measured separation of component 1 of H_α and D_α, in air, is $\Delta s=(4.1453\pm0.0010)$ cm^{-1}. This becomes 4.14415 ±0.0010 cm^{-1} in vacuum, as contrasted with Williams' 4.14691 cm^{-1} and with Houston's preliminary values[39] of 4.1440 and 4.1399 cm^{-1}. Accepting Robinson's estimate of his own probable error in Δs, and using the probable error in F already given, we obtain

$$E=(5.4864_4\pm0.0013_2)\times10^{-4}$$

and

$$e/m=(1.7591_4\pm0.00046)\times10^7.$$

The resulting probable error in e/m is essentially that *adopted* for Williams' result, and the data just given thus show directly the error one needs to assume in the $H_\alpha-D_\alpha$ interval to get my adopted error in e/m. I assume the same accuracy for the work of Williams and of Robinson and *adopt* for Robinson's result

$$e/m=(1.7591_4\pm0.0005)\times10^7.$$

c. Work of Shane and Spedding

The last investigation on the fine structure of H_α and D_α to be discussed, but the earliest in point of time, is that of Shane and Spedding.[40] They used an interferometer with a plate separation of about 7.8 mm. They make an elaborate analysis of their intensity curves, and give their final separations of H_α and D_α components in terms of orders of interference, but not in terms of wave-length or wave number. Each result is accompanied by its corresponding value of e/m. Under the circumstances the simplest procedure appears to be merely to accept their final average value of e/m, which is $(1.7579\pm0.0003)\times10^7$, and then correct it for the change in values of auxiliary constants. They used Eq. (12) and in this equation their adopted values give $F(D-H)/H^+D=4786.383$, whereas my present adopted values give 4785.7526. The value of e/m is then to be reduced in this ratio. But according to Williams and Gibbs,[36] Shane and Spedding did not reduce their wave number interval from air to vacuum, although in Eq. (12) they used the wave number in vacuum of R_H. To correct for this error, one should multiply their result by the index of refraction of air (1.000276), thus giving 1.0001444 as the resulting factor for the two almost compensating corrections. The revised result, with my own adopted probable error, is

$$e/m=(1.7581_5\pm0.0006)\times10^7 \text{ e.m.u.}$$

Experimental Values of e/m by Other Methods

In 1938 I obtained,[22] as the best average value of e/m from all methods, $(1.7591\pm0.0003)\times10^7$ abs. e.m.u. The first four determinations listed then comprise the work on H, D, and He^+, and revised values for all four have now been ob-

[38] C. F. Robinson, Phys. Rev. **55**, 423A (1939).
[39] W. V. Houston, Phys. Rev. **51**, 446 (1937).
[40] C. D. Shane and F. H. Spedding, Phys. Rev. **47**, 33 (1935).

tained, together with the new value by DRW.[6] The remaining six determinations given in the 1938 letter, together with one new determination, will now be considered. No attempt is made at critical discussion, and in fact my only object now is to explain, as briefly as possible, why my present adopted value, or its assigned probable error, deviates from that given by the author. In general it is difficult, in the case of the methods now to be considered, for an outsider to make any intelligent evaluation of the probable error, and hence I have, in general, merely accepted that published by the author. It is quite possible that, *relative* to the adopted probable errors in the preceding sections of the paper, all of the probable errors to follow should be slightly increased.

When e/m is obtained from fine structure analysis, the value of $F_i q$ is involved, where F_i is the value of the Faraday in international electric units, and $F(=F_i q)$ its value in absolute units. Now as already discussed in footnote 23, I have, subsequent to the 1938 work[22] on e/m, *raised* the value of F_i and *lowered* that of q by almost equal amounts. Hence the resulting values of e/m are virtually unchanged, although additional small changes have now been made in certain instances. On the other hand, in the case of five of the six remaining methods that have been used in a precise determination of e/m, F_i does not appear at all in the equation, but q appears in the denominator. Hence in all these cases e/m is *raised* by about 0.00012×10^7 e.m.u., as a result of the *lowering* of q from 0.99993 to 0.99986. In the sixth method (refraction of x-rays), $F_i q$ occurs in the denominator and again the value of e/m is virtually unchanged.

a. Zeeman effect

A number of investigations on the value of e/m from Zeeman effect have been carried out by Houston and co-workers. The results of all of their work are tabulated by Kinsler and Houston.[41] These comprise the final results of work on Zn, Cd, He, and Ne. They give as a final weighted average, $e/m=(1.7570\pm0.0007)\times10^7$. It is not apparent how the probable error was obtained. Accepting their own probable errors for the four individual results, I obtain as the weighted average $1.7569_{46}\pm0.00017$ by external consistency, and ±0.00047 by internal consistency. Since, however, it is well to make some allowance for systematic errors, I will increase this latter error to ±0.0007, to agree with their own assigned error. The values of the auxiliary constants are not stated, but in an earlier paper[42] the values $q=0.99995$ and $c=299{,}796$ km/sec. were used, and I believe were used also in all succeeding papers of the series. In 1934 I recommended[43] $c=299{,}776\pm4$ km/sec., and the inclusion of more recent results leaves unchanged both this average and its probable error. In the Zeeman effect work the change in c decreases e/m by almost the same amount that the change in q increases it. The exact corrected result is 1.7569_{87}. Hence I adopt

$$e/m=(1.7570\pm0.0007)\times10^7 \text{ e.m.u.}$$

b. Refraction of x-rays

Bearden,[44] in an elaborate investigation, obtained $e/m=(1.7601\pm0.0003)\times10^7$. All of his auxiliary constants agree with those I was using at the time. Hence the only essential change now to be made is that resulting from the very small changes in F and C. His stated probable error is very small, but is the result of a detailed consideration of the errors of all factors in the final expressions for e/m. His exact probable error in e/m, based on $F=9651.3\pm0.80$, is $\pm0.0003_{17}$. With the new $F=9651.4_0\pm1.0$ and $C=12.01465\pm0.00023$, his result becomes $1.7600_6\pm0.0003_3$. In order to make at least a slight allowance for systematic error I *adopt*

$$e/m=(1.7600_6\pm0.0004)\times10^7 \text{ e.m.u.}$$

c. Direct velocity measurements

Two careful investigations by this method have been made, the first by Perry and Chaffee,[45] and the second by Kirchner.[46] Perry and Chaffee obtained six series of results, with an actual average of 1.7609 ± 0.0002, where the error is

[41] L. E. Kinsler and W. V. Houston, Phys. Rev. **46**, 533 (1934).

[42] J. S. Campbell and W. V. Houston, Phys. Rev. **39**, 601 (1932).

[43] R. T. Birge, Nature **134**, 771 (1934).

[44] J. A. Bearden, Phys. Rev. **54**, 698 (1938).

[45] C. T. Perry and E. L. Chaffee, Phys. Rev. **36**, 904 (1930).

[46] F. Kirchner, Ann. d. Physik **8**, 975 (1931) and **12**, 503 (1932).

TABLE I.

e/m	P. E.	REFERENCE IN TEXT	METHOD	$f(F_i pq)$
1.75913	3.7×10^{-4}	6	H_α and D_α	$F_i q$
1.75797	5.0×10^{-4}	1	H_α and D_α	$F_i q$
1.75914	5.0×10^{-4}	38	H_α and D_α	$F_i q$
1.75815	6.0×10^{-4}	40	H_α and D_α	$F_i q$
1.76048	5.8×10^{-4}	3, 28	R_H and R_{He}	$F_i q$
1.75700	7.0×10^{-4}	41	Zeeman effect	$1/q$
1.76006	4.0×10^{-4}	44	X-ray refraction	$1/F_i q$
1.76110	10.0×10^{-4}	45	Direct velocity	$1/pq$
1.75900	9.0×10^{-4}	46	Direct velocity	$1/pq$
1.75982	4.0×10^{-4}	48	Magnetic deflection	$1/q$
1.75820	13.0×10^{-4}	49	Crossed fields	p/q
1.75870	8.0×10^{-4}	51	Busch method	p/q

based on external consistency. They however *adopt* a final probable error of ±0.0010, and I shall do the same. The value of c enters into their formula in a rather complex way and I find, by actual trial, that the change of c from 299,796 to 299,776 produces a change in e/m of only about one part in 10^5, which is negligible. They used $pq=1.00046$ to reduce from int. to abs. volts, and with the new value 1.00034, one gets $e/m=1.7611_1$. I therefore *adopt*

$$e/m=(1.7611\pm0.0010)\times10^7 \text{ e.m.u.}$$

Kirchner[46] obtained, in two separate investigations, 1.7585 ± 0.0012 (revised from the original 1.7598 ± 0.0025) and 1.7590 ± 0.0015. From these results I obtained[47] a weighted average of 1.7587 ± 0.0009, where the error is based on internal consistency. This average has since been quoted in the literature as Kirchner's final result. Kirchner gives corresponding figures in int. and abs. volts that imply an assumed $pq=1.0005$. With our new value, the weighted average becomes 1.7589_6 and I *adopt*

$$e/m=(1.7590\pm0.0009)\times10^7 \text{ e.m.u.}$$

d. Magnetic deflection

Using a new magnetic deflection method devised by E. O. Lawrence, Dunnington[48] has made a most extensive and refined investigation of the value of e/m. His final published result is 1.7597 ± 0.0004. This result is based on $q=0.99993$. With the new value of q one obtains

$$e/m=(1.7598_2\pm0.0004)\times10^7 \text{ e.m.u.},$$

which I adopt.

e. Crossed fields

Shaw[49] has used a method of crossed electric and magnetic fields to obtain a published value of $e/m=1.7571\pm0.0013$. He, however, failed to make the reduction from international to absolute electric units, and since the factor V/H^2 appears in his equation (V=potential difference, H=magnetic field), the proper reduction factor is $pq/q^2=p/q=1.00062$ for the values of p and q now chosen. Hence his corrected result is

$$e/m=(1.7582\pm0.0013)\times10^7 \text{ e.m.u.},$$

which I adopt.

f. Longitudinal magnetic field (Busch method)

In 1929 the best work on e/m with the Busch method was that by Wolf.[50] His investigation is discussed on pp. 43–44 of G.C.1929. At that time I assumed that he had not made the correction from international to absolute units, an assumption that was later verified. As in the case of crossed fields, the factor V/H^2 again appears in the equation. In 1929 I corrected Wolf's result from 1.7679 to 1.7689. With the latest p/q value, it becomes 1.7690.

A recent and much more accurate determination by this method has been made by Goedicke.[51] He does not give the values of p and q used, but from certain published figures, his value of q is evidently about 0.99991. I assume that his value of p is 1.00050, since that value is commonly used. On these assumptions, his value of $e/m=1.7586$ should be raised only to 1.7587. He gives 0.0023 as a *maximum* possible error, and following my usual custom I will take 1/3 of this as the probable error. Hence I adopt

$$e/m=(1.7587\pm0.0008)\times10^7 \text{ e.m.u.}$$

for his final result.

SUMMARY OF VALUES OF e/m

We have now discussed and adopted values of e/m from twelve different investigations, covering seven essentially different methods. All of the adopted results and probable errors are listed in Table I. So far as values of the auxiliary constants

[47] R. T. Birge, Phys. Rev. **42**, 736 (1932).
[48] F. G. Dunnington, Phys. Rev. **43**, 404 (1933) and **52**, 475 (1937).
[49] A. E. Shaw, Phys. Rev. **54**, 193 (1938).
[50] F. Wolf, Ann. d. Physik [4] **83**, 849 (1927).
[51] Egon Goedicke, Ann. d. Physik [5] **36**, 47 (1939).

are concerned, the chief sources of recent change and controversy are the values of F_i (the Faraday in international units), p and q. The last column shows the explicit dependence of e/m on these three constants.

The weighted average of the 12 results is $e/m=1.75920_6$. The probable error by external consistency (r_e) is 0.00019_2, and by internal consistency (r_i) is $\pm 0.00015_8$. The ratio r_e/r_i is 1.213, which is very satisfactory. In 1938 I got[22] for the corresponding results 1.75909 ± 0.00024 (r_e) and $r_e/r_i=1.51$, and recommended 1.7591 ± 0.0003 as the best value to adopt. Although the new average (1.75920_6) is only slightly larger than the value 1.7591, which has been rather widely used for the past three years, it seems best to adopt it.

It is, however, desirable to consider in some detail the internal consistency of the data since, as noted in my 1938 paper,[22] this is a subject that has been under discussion for many years. In that paper I concluded that the annoying previous discrepancy between the "spectroscopic" and the "deflection" values of e/m had virtually disappeared. Bearden[52] definitely disagreed with this conclusion, and even disagreed with my classification of his x-ray refraction value of e/m as a "spectroscopic" result. So far as this last point is concerned, I think it is mainly a question of how the two groups of results are defined.

Although in 1929[2] I gave *two* values of e/m, commonly referred to as the "spectroscopic" and the "deflection" values, I never for one moment believed that there are actually two different values. I assumed then, and I still assume, that any apparent discrepancy is due to errors of theory or of experiment, or both. Certain values of e/m are obtained with spectroscopic equipment and involve measurements of spectral wavelengths. These I have grouped together to obtain a weighted average "spectroscopic" result, and Bearden's result certainly belongs in this class. The other experiments are electric and magnetic in character, and involve linear acceleration and deflection of free electrons over comparatively long paths. The technique and quantities measured are totally different from those in the spectroscopic work. Hence the systematic errors are also likely to be totally different, and to such errors I attribute any outstanding difference in the values of e/m that may exist.

Bearden[52] gives a rather close argument to show that his value of e/m is concerned with "free" electrons, and hence should be classed with the deflection experiments. With this assumption he gets two values of e/m ($1.7583_1 \pm 0.0002_8$ and $1.7598_8\pm 0.0001_7$), and he states that there is less than one chance in 10^9 of such a discrepancy being due to chance. His data, however, give for the discrepancy 0.00157 ± 0.0003276, or 4.79 times its probable error, and there is one chance in 826 of this occurring. If these last odds are taken at face value, a really serious discrepancy exists, but there seems to be no point in exaggerating the situation.

In considering the question now, I will omit Bearden's x-ray result from *both* groups. Then the first six results in the table comprise the spectroscopic group, and these six give

$$e/m=1.75880\pm 0.00028_{20}\ (r_e)$$
$$\text{or}\quad \pm 0.00020_{81}\ (r_i) \qquad \text{ratio } 1.355,$$

whereas the last five results of the table comprise the deflection group, and give

$$e/m=1.75959\pm 0.00024_{07}\ (r_e)$$
$$\text{or}\quad \pm 0.00030_{65}\ (r_i) \qquad \text{ratio } 0.785.$$

With the probable errors based on external consistency (r_e), there is one chance in $6\frac{2}{3}$ that this discrepancy is accidental (the discrepancy being 2.13 times its probable error), and an almost identical result is obtained from the r_i values. Although one would naturally wish that the odds were more nearly even, a discrepancy of this magnitude is not considered by statisticians as of any real significance.

If now we compare Bearden's result (point 7 of the table), with the two averages just found, and use r_e errors, we find that the odds are just even that his result is consistent with the deflection average, but there is only one chance in 12 that his result is consistent with the spectroscopic average. One possible conclusion from these facts is that point 7 is definitely too high. It is, however, worth while to explore the matter further.

[52] J. A. Bearden, Phys. Rev. **55**, 584 (1939).

It has already been mentioned in footnote 23 that the value of F now adopted is almost identical with that advocated in 1938, but the coincidence is only accidental, and is actually the result of two almost compensating changes that have been made.

Since F appears in different equations for e/m in different positions, it is possible to *evaluate* it merely from the e/m data. The resulting value has, however, a larger probable error than the value obtained from electrolysis. Thus the weighted average of points 1–5 inclusive is $e/m=1.75897\pm0.00026_{45}$ (r_e) or $\pm0.00021_{79}$ (r_i). The ratio r_e/r_i is 1.21_4, which is satisfactory. If now we calculate the value of F that will bring this result into agreement with Bearden's point 7, the result is

$$F=9651.40(1.76006/1.75897)^{\frac{1}{2}}$$
$$=9654.39 \text{ abs. e.m.u.},$$

and the new value of e/m is $[(1.76006)(1.75897)]^{\frac{1}{2}}=1.7595_{15}$. This is very close to the "deflection" average of 1.75959, which does not involve F at all. In fact, the value of F that will force the fine structure average (1.75897) to agree with the deflection average is

$$F=(9651.40)(1.75959)/(1.75897)$$
$$=9654.80 \text{ abs. e.m.u.}$$

The two new values of F just computed correspond to 96,531 and 96,535 int. coulombs (chemical scale), values that are far above the direct results given by either the silver voltameter (96,494) or the iodine voltameter (96,511). Such high values of F are clearly ruled out, on the basis of all experimental work with voltameters, but it is certainly worth noting that the value $F=96{,}533$ int. coulombs (chemical scale) will bring into almost perfect agreement *all* values of e/m, except that from Zeeman effect (point 6), which is certainly too low.

My final conclusion is then that, on the basis of all experimental work to date, 1.7592 is the best value of e/m. But if it becomes possible, as a result of the future discovery of new sources of systematic error in F, to raise its value some 30 coulombs above the present adopted result of 96,501.3 int. coulombs (chemical scale), then the consistency of the present e/m results will be greatly improved, and the best value of e/m will become 1.7595 or 1.7596. The weighted average of all 12 results, as already given, is $1.7592_1\pm0.0002$, but just because of this possible uncertainty in regard to the value of F, I shall enlarge the probable error to 0.0005. Hence the final *recommended* value is

$$e/m=(1.7592\pm0.0005)\times10^7 \text{ abs. e.m.u.}$$

or

$$(e/m)c=(5.2736_6\pm0.0015)\times10^{17} \text{ abs. e.s.u.}$$

Then, from the adopted values of e/m and F

$$E=(5.4862_4\pm0.0017)$$
$$\times10^{-4} \text{ (physical scale) (derived).}$$

Summary

As a matter of convenience, the final values adopted in this paper are now listed. A list of adopted values of auxiliary constants has already been given, as well as the individual values of e/m. All of the following results are based entirely on the work of DRW,[6] except the value of e/m and the derived value of E.

$R_H=109{,}677.581_2\pm0.007_5$ cm^{-1} (I.A. scale),
$R_D=109{,}707.419_3\pm0.007_5$ cm^{-1} (I.A. scale),
$R_{He}=109{,}722.263\pm0.012$ cm^{-1} (I.A. scale),
$R_\infty=109{,}737.303\pm0.017$ cm^{-1} (I.A. scale),
or ±0.05 cm^{-1} (c.g.s. system),
$e/m=(1.7592\pm0.0005)\times10^7$ abs. e.m.u.,
$(e/m)c=(5.2736_6\pm0.0015)\times10^{17}$ abs. e.s.u.,
$E=(5.4864_7\pm0.0009_9)$
$\times10^{-4}$ (physical scale) (direct),
$E=(5.4862_4\pm0.0017)$
$\times10^{-4}$ (physical scale) (derived).

In general calculations, the *derived* value of E should be used, in order that it may be consistent with the adopted values of F and e/m.

Further Resolution of Two Parallel Bands of Ammonia and the Interaction between Vibration and Rotation

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The fundamental low frequency parallel band at 10μ and its upper stage band at 16μ have been re-examined under high dispersion. It is found that most of the fine structure lines hitherto reported as single are resolved into multiplets. The positions of the lines may be accounted for accurately by assuming that the energy levels have the form,

$$W^{s,a}/hc = W_V^{s,a}/hc + A_V^{s,a}(J^2+J-K^2) + C_V^{s,a}K^2 + F(JK).$$

The superscripts s or a indicate whether the level in question is the lower or the upper of the two levels produced by the double minimum potential. $F(JK)$ is the small centrifugal distortion term calculated by Slawsky and Dennison. The constants A_0^s, A_0^a, A_1^s, A_1^a, A_2^s, $C_1^s - C_0^a$ and $C_1^a - C_0^s$ are determined from the experimental data. The following vibrational energies are also found, $W_1^s = 932.24hc$, $W_1^a = 968.08hc$ and $W_2^s = 1597.4hc$.

In the discussion of the rotational constants, it is pointed out that two quantities are involved, (a) the average constants, averaged over the two levels of the double minimum, as $\frac{1}{2}(A_v^s + A_v^a)$, and (b) the difference of the constants, as $A_v^a - A_v^s$. Recently Shaffer has calculated the theoretical expressions for the averaged constants and has shown how these depend upon the anharmonic terms in the potential energy. A treatment of the difference of the constants is equivalent to a treatment of the change in the splitting of the two levels of the double minimum due to the vibration-rotation interaction. This may be computed from the expression for the splitting of the double minimum levels given by the W-K-B method of approximation. The calculated result for the change in splitting of the first vibration levels is

$$(\delta\Delta/hc)_{\text{theo}} = -0.162(J^2+J) + 0.222K^2,$$

which is in excellent agreement with the observed change

$$(\delta\Delta/hc)_{\text{exp}} = -0.17(J^2+J) + 0.23K^2.$$

The significance of the agreement is discussed.

INTRODUCTION

THE general problem of the evaluation of the vibration-rotation energy levels of polyatomic molecules has received considerable attention in recent years and much progress has been made. The present paper contributes to this problem and is concerned with the high resolution of the low frequency parallel bands of ammonia. It will be shown that certain novel features appear here which are produced by the double minimum potential of ammonia and which are not likely to occur in measurable degree in other spectra.

The Hamiltonian function representing a polyatomic molecule is separable only in zeroth approximation and the usual procedure is to develop H as a series involving a number of orders of approximation and to treat these by the methods of perturbation theory. In zeroth approximation the vibration-rotation energy levels of an axially symmetrical molecule, such as ammonia, are given by the expression,

$$W_0/hc = \sum_i \omega_i(V_i + \tfrac{1}{2}d_i) + A_e(J^2+J) + (C_e - A_e)K^2.$$

Here the ω_i are the normal vibration frequencies (expressed in cm^{-1}) and d_i are the degrees of degeneracy of the various normal vibrations.

$$A_e = h/8\pi^2 c I_A^0, \quad C_e = h/8\pi^2 c I_C^0,$$

where I_A^0 and I_C^0 are the equilibrium values of the moments of inertia for axes perpendicular to and parallel to the symmetry axis, respectively.

When the change of the electric moment due to the vibration lies along the symmetry axis, the selection rules for the rotational numbers are $\Delta J = 0, \pm 1$ and $\Delta K = 0$. As is well known this produces a simple band of the so-called parallel type which consists of a positive, negative and zero branch. The lines of the positive and negative branches have the spacing $2A_e$ and are multiple, that is, each line is composed of a number of superimposed components. It is to be expected that in the next order of approximation these component lines may separate slightly from each other.

In the case of the ammonia molecule there is one further circumstance to be recalled.[1] The

[1] For a review of the ammonia spectrum see D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

nitrogen atom possesses two equivalent positions of equilibrium, one on either side of the plane of the hydrogens. This fact produces a splitting of each energy level into two levels. The doublet separation is small (about 0.66 cm^{-1}) for the ground state but becomes rapidly larger for the excited states of the vibration ν_3. The wave functions characterizing these two states are either symmetrical or antisymmetrical with respect to the plane of the hydrogen atoms, the lower of the two levels of the doublet being symmetrical. Parallel type bands, such as those to be discussed here, correspond to transitions connecting a symmetrical with an antisymmetrical level.

The methods for treating the interaction between the vibration and rotation of polyatomic molecules have been discussed by Wilson and Howard[2] and have recently been applied in detail to the pyramidal XY_3 molecule by Shaffer.[3] This treatment leads to an expression of the following type for the energy of a level not involving a perpendicular vibration.[4]

$$W^s/hc = W_V{}^s/hc + A_V{}^s(J^2+J) + (C_V{}^s - A_V{}^s)K^2 + F(JK). \quad (1)$$

The first term $W_V{}^s$ represents the vibrational energy. The quantities $A_V{}^s$ and $C_V{}^s$ are functions of the vibrational numbers, in first approximation linear functions. The superscript s indicates that the level in question is the lower member of the doublet pair caused by the double minimum character of the potential; the upper level will be designated with the superscript a. Shaffer's formula does not contain the superscript s or a, of course, since he did not consider effects arising from the double minimum potential.

The fact that $A_V{}^s$ and $A_V{}^a$ may differ from each other is indicated by the following qualitative argument. Consider the case where $K=0$. This corresponds to the classical motion in which the molecule is rotating about an axis perpendicular to the axis of the pyramid. The centrifugal force tends to force the hydrogen atoms away from the nitrogen and to make the apex angle of the pyramid more acute. In other words the centrifugal distortion *raises* the barrier separating the two equivalent equilibrium positions of the nitrogen atom. Accordingly, the doublet separation, which is a very sensitive function of the barrier height, will be decreased and therefore $A_V{}^a - A_V{}^s$ must be negative. On the other hand when $K=J$ the energy levels correspond to the classical motion of rotation about the axis of the pyramid. The centrifugal forces will clearly tend to make the apex angle of the pyramid more obtuse and hence in effect will *lower* the barrier height. Thus we may expect $C_V{}^a - C_V{}^s$ to be positive. It will appear that the experimental data are in accord with these predictions.

The last term in Eq. (1), namely $F(JK)$, represents what may be called the centrifugal distortion of the molecule. It is small, depends principally upon quartic combinations of the quantum numbers J and K and is in first approximation independent of the vibrational state; hence no superscript s or a is necessary. $F(JK)$ has been calculated by Slawsky and Dennison.[5] Recently Foley and Randall[6] have measured under high dispersion lines of the pure rotation spectrum of ammonia. They were thus able to determine $F(J,K)-F(J-1,K)$ experimentally and their results are in almost perfect agreement with the calculated formula, particularly when the new values of the molecular force constants[1] are used.

$$F(J,K) - F(J-1,K) = -0.00294J^3 + 0.00279JK^2. \quad (2)$$

The frequencies of the lines constituting a parallel type band may be written out easily from the energy expression Eq. (1). For example, the positive branch lines of the band corresponding to the change $0_s \rightarrow 1_a$ in the vibrational number are given by

$$\nu^{0,s,J-1,K}_{1,a,J,K} = (W_1{}^a - W_0{}^s)/hc + (A_1{}^a + A_0{}^s)J + (A_1{}^a - A_0{}^s)J^2 + (C_1{}^a - C_0{}^s - A_1{}^a + A_0{}^s)K^2 + F(J,K) - F(J-1,K). \quad (3)$$

[2] E. B. Wilson and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).
[3] W. H. Shaffer, J. Chem. Phys. **9**, 607 (1941).
[4] In the case of the perpendicular frequencies there occur additional terms due to the Coriolis forces.
[5] Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. **7**, 509 (1939).
[6] H. M. Foley and H. M. Randall, Phys. Rev. **59**, 171 (1941).

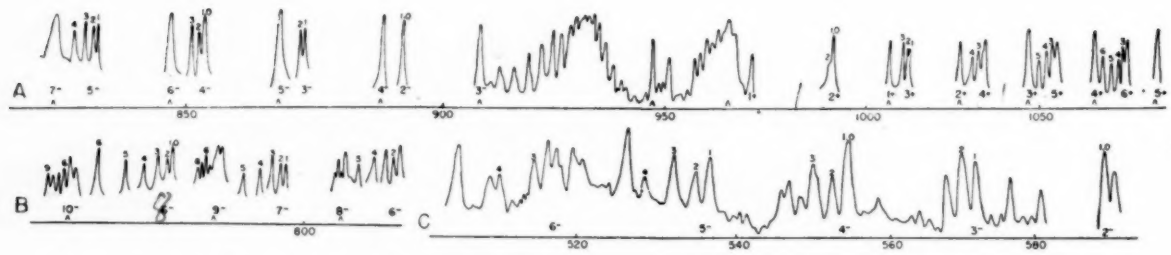

FIG. 1. Curves *A* and *B*: The double 10μ band with partially resolved *Q* branches. The $0_s \rightarrow 1_a$ component with center at 968.08 cm^{-1} is marked A. Center of the $0_a \rightarrow 1_s$ band lies at 931.58 cm^{-1}. Curve *C*: A part of the *P* branch of the 16μ band $1_a \rightarrow 2_s$.

Thus the fact that the quantities A and C are functions of the vibrational state introduces a convergence in the series through the term proportional to J^2. Moreover since K may take on the values, 0, 1, $\cdots$, $J-1$, each line which was formerly single will be split into a multiplet of J components. The spacing of the lines in a multiplet will be quadratic. Since, as has been pointed out, the A and C depend upon whether the superscript is s or a, the convergence and the multiplet spacing of the complementary vibrational band $0_a \rightarrow 1_s$ may be very different from that of the band $0_s \rightarrow 1_a$. The intensities of lines in a multiplet are interesting. Because of the proton spin, when K is a multiple of three the line in question is enhanced by the factor two. The state where $K=0$, J is even and the vibration superscript is s does not exist and consequently lines involving a transition to it are absent. Likewise, states where $K=0$, J is odd and the superscript is a do not occur.

The bands which have been chosen for the present investigation are the long wave parallel bands corresponding to the following changes in the vibrational quantum number V_3, $0_s \rightarrow 1_a$, $0_a \rightarrow 1_s$ and $1_a \rightarrow 2_s$. The first two bands lie at about 10μ while the third has its center at about 16μ. The next section describes the experimental procedure and results, and shows that the observed lines may be adequately represented by means of a formula of the type of Eq. (3). In the last section an attempt is made to calculate $(A_{V^a} - A_{V^s})$ and $(C_{V^a} - C_{V^s})$ theoretically.

EXPERIMENTAL[7]

The spectrometer employed for these observations has already been described.[8] For the 10μ band an absorption cell 12 cm long with KBr windows was found convenient. The gas pressures ranged from 2 to 5 cm. The resolving power was about 1000 with the slit widths used (about 0.45 mm, corresponding to 0.35 cm^{-1}). For the weaker 16μ band, a cell having an absorption path of two meters was available. Because of its small aperture much wider slits (about 0.9 mm) were necessary, and the resolving power was somewhat less.

The results are shown in Fig. 1. The upper curve is the double 10μ band, its high frequency component, namely $0_s \rightarrow 1_a$, being indicated with A. The lower curve is the negative or *P* branch of the 16μ band ($1_a \rightarrow 2_s$ transition). It is considerably obstructed by many water lines. The positive or *R* branch of this band is not accessible on account of the strong absorption of atmospheric CO_2. The numbers below the lines in the figure are the initial J values, and those above the lines are the K values. The line frequencies, measured in wave numbers reduced to vacuum, are given in Table I.

A study of Fig. 1 reveals that the 10μ band possesses all the qualitative features predicted by Eq. (3). The lines of this parallel type band are clearly multiple and the multiplet spacing is very different for the band $0_a \rightarrow 1_s$, where it is large, and for the band $0_s \rightarrow 1_a$ where it is so small as to be observable only in the lines of higher ordinal number. The enhancement of the lines where K is a multiple of three is also clear, but the absence of half of the lines where $K=0$ is less apparent since the resolution of the spec-

[7] During the spring of 1936, Dr. M. V. Migeotte working in this laboratory mapped a part of the positive branch of the 10μ band, and was able to resolve the fine structure of a number of the lines. His results were in substantial agreement with those we have obtained. We wish to acknowledge his priority in resolving this portion of the band, and to thank him for allowing us to examine his measurements.

[8] J. D. Hardy, Phys. Rev. **38**, 2162 (1931).

trometer is not sufficient to distinguish between the lines $K=0$ and $K=1$. However, a study of the positions of the lines shows without question that the theoretically predicted missing lines are indeed absent. Specifically, the separation between the line $K=2$ and the first line of the multiplet, which is either the single line $K=1$ or the merged line of $K=0$ and $K=1$, is systematically larger in the latter case.

The quantitative treatment of the data is not difficult. It is desired to show (a) whether the energy levels may be expressed in the form given by Eq. (1), and (b) to evaluate the constants A_V^s, A_V^a, C_V^s and C_V^a. The first step is to eliminate the centrifugal distortion term $F(JK)$. This may be done by subtracting the numerical values given by formula (2) from the observed line positions of the positive branch and adding them to the line positions of the negative branch. One thus obtains lines corresponding to a fictitious molecule which possesses a vibration rotation energy expression in which the centrifugal distortion term $F(JK)$ has been omitted. The second step is to use the combination relation to obtain the difference in energy between two states of the molecule having the same vibrational excitation, 1_s or 1_a, the same K but with values of J differing by two units. From these

TABLE I. *Observed positions of lines in the bands at 10μ and 16μ.*

TRANSITION	R BRANCH J	R BRANCH K	R BRANCH ν_{vac}	P BRANCH J	P BRANCH K	P BRANCH ν_{vac}
$0_a \rightarrow 1_s$	5→6	3	1053.11	2→1	0,1	892.05
		4	1051.42	3→2	1	872.52
	4→5	3	1032.05		2	871.70
	3→4	1	1013.06	4→3	0,1	853.66
		2	1012.47		2	852.70
	2→3	0,1	992.55		3	851.30
				5→4	1	834.73
					2	833.96
					3	832.61
					4	830.60
				6→5	0,1	816.48
					2	815.55
					3	814.13
					4	812.53
					5	809.68
$0_s \rightarrow 1_a$	5→6		1084.59	1→0		948.21
	4→5		1065.49	3→2		908.15
	3→4		1046.34	4→3		887.93
	1→2		1007.51	5→4		867.80
				9→8	6	783.39
					7	782.75
					8	782.14
				10→9	6	763.55
					7	762.87
					9	761.35
$1_a \rightarrow 2_s$	2→1	0,1	590.32	5→4	1	536.14
	3→2	1	571.41		2	534.74
	4→3	0,1	553.96		3	531.99
		2	551.93		4	528.49
				6→5	3	515.38

TABLE II. *Values of constants A_1.*

J	K	$2A_1^s$	J	$2A_1^a$
5→6, 5→4	3	20.111	5→6, 5→4	19.780
	4	20.121	4→5, 4→3	19.772
4→5, 4→3	3	20.120	3→4, 3→2	19.773
3→4, 3→2	1	20.113	1→2, 1→0	19.773
	2	20.137		
2→3, 2→1	0,1	20.116	Average	19.774
	Average	20.120		

$2A_1^s$ or $2A_1^a$ are found by dividing by $(2J+1)$. The results of this procedure are shown in Table II. Note that in the case of the band $0_s \rightarrow 1_a$, which determines $2A_1^a$, the multiplet spacing is so small that up to $J=6$ the lines are observed as single. It is seen that the various determinations of $2A_1^a$ and $2A_1^s$ are quite consistent although the last figure in the average values is no doubt meaningless.

In a similar way the combination relations may be used to determine the $2A_0^s$ and $2A_0^a$; these are given in Table III.

The spacings of the lines composing a given multiplet furnish the means of determining such quantities as $(C_1^s - C_0^a - A_1^s + A_0^a)$. The procedure of course is to divide by $2K+1$ the interval between two lines having the same J but with K values differing by unity. The results appear in Table IV.

For the 16μ band which corresponds to the vibrational transition $1_a \rightarrow 2_s$, it is not possible to use combination relations since only one branch could be measured experimentally. However, since the energies of the 1_a levels are known, those of the 2_s levels may be found. From them the following numerical values are obtained:

$$2A_2^s = 20.36,$$
$$C_2^s - C_1^a - A_2^s + A_1^a = -0.50.$$

Finally the centers of each of the three bands may be located with considerable precision. The interval between the ground levels 0_s and 0_a is taken from observations of Wright and Randall.[9]

$$W_0^s/hc = 0,$$
$$W_0^a/hc = 0.66,$$
$$W_1^s/hc = 932.24,$$
$$W_1^a/hc = 968.08,$$
$$W_2^s/hc = 1597.4.$$

[9] N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).

TABLE III. *Values of constants* A_0.

J	K	$2A_0^a$	J	$2A_0^s$
6→5, 4→5	3	19.876	5→4, 3→4	19.887
5→4, 3→4	1	19.873	3→2, 1→2	19.890
	2	19.884		
4→3, 2→3	0,1	19.877	Average	19.888
	Average	19.877		

It will appear in the next section that certain combinations of A and C are susceptible of theoretical estimation. For convenience we list these below. The data do not seem to warrant the retention of more than two significant figures.

$$A_0^a-A_0^s=-0.00_5,$$
$$A_1^a-A_1^s=-0.17,$$
$$(C_1^a-C_0^s-A_1^a+A_0^s)-(C_1^s-C_0^a-A_1^s+A_0^a)$$
$$=0.23\cong(C_1^a-C_1^s)-(A_1^a-A_1^s).$$

In the next section it will be shown that there are theoretical arguments for supposing that both $A_0^a-A_0^s$ and $C_0^a-C_0^s$ are small. Experimentally $A_0^a-A_0^s$ is indeed small and it is safe to conclude that $C_0^a-C_0^s$ is also negligible. Hence the approximation in the last equation is probably quite good and $C_1^a-C_1^s=+0.06$.

The experimental data and their analysis appear to be very satisfactory. The consistency shown in Tables II, III, and IV demonstrates that these vibration rotation energy levels of the ammonia molecule may be expressed by a formula of the type of Eq. (1). Moreover the qualitative predictions regarding the effect of centrifugal forces upon the rotational constants A and C are verified since $A_1^a-A_1^s$ is observed to be negative, whereas $C_1^a-C_1^s$ is positive.

DISCUSSION

In considering the interaction between vibration and rotation it is best to divide the effects into two classes: (a) the effects which are independent of the double minimum nature of the potential energy, and (b) effects which may be attributed solely to the double minimum potential. Of these, the former will determine the average values of A and C (averaged over the two levels caused by the double minimum), that is, $\frac{1}{2}(A_V^s+A_V^a)$ and $\frac{1}{2}(C_V^s+C_V^a)$. The latter will fix the interval between the two levels of any pair resulting from the double minimum. From Eq. (1), this separation, $\Delta\nu$, is given by

$$\Delta\nu/hc=(W_V^a-W_V^s)/hc$$
$$+(A_V^a-A_V^s)(J^2+J-K^2)+(C_V^a-C_V^s)K^2.$$

(a) The methods of treating the vibration-rotation interactions which are independent of the double minimum potential are well known and, as already stated, have been applied in detail to the pyramidal molecule XY_3 by Shaffer.[3] They consist in developing the Wilson and Howard form of the Hamiltonian in a series of approximations and of treating each term by perturbation theory. This procedure does not distinguish between the levels s and a and consequently will describe the average values of the A and C for these levels. Shaffer finds, essentially,

$$\tfrac{1}{2}(A_V^s+A_V^a)=A_e-\sum\alpha_i(V_i+\tfrac{1}{2}d_i),$$
$$\tfrac{1}{2}(C_V^s+C_V^a)=C_e-\sum\gamma_i(V_i+\tfrac{1}{2}d_i).$$

The subscript i ranges over all the normal frequencies and the V_i are the corresponding quantum numbers. The quantities α_i and γ_i are functions of the masses, the normal frequencies and of those anharmonic terms in the potential which are cubic in the normal coordinates. There are eight of these unknown cubic constants and it is thus evident that the fine structures of at least eight of the ammonia bands must be measured before this part of the problem can be solved in detail. Before turning our attention to (b) we may remark that the average values of A_V and C_V depend essentially upon the potential function in the neighborhood of the equilibrium configuration, that is upon the region where the wave function is large. On the other hand, the doublet separation is determined by the behavior of the potential near the barrier. A study of the doublet separation is thus capable of furnishing information about the molecule at points which are distant from the equilibrium configuration.

(b) Since the Hamiltonian function proposed by Wilson and Howard is exact, it might furnish a starting point for the calculation of $A_V^a-A_V^s$ and $C_V^a-C_V^s$. It is very complicated however and the particular series development used in (a) would probably not be applicable here. Certain approximations may be made which greatly

simplify the work and which appear to be well justified physically. The principal assumption is that the normal coordinate x_3 associated with the band ν_3 at 10μ, leads directly over the lowest part of the pass connecting the two equivalent equilibrium configurations of the molecule. This assumption must be very nearly true since it is known experimentally that the doublet separations for the excited states of the vibrations ν_1, ν_2 and ν_4 differ only slightly, if at all, from the doublet separation 0.66 cm^{-1} of the ground state. On the other hand, the doublet separation of the first excited state of ν_3, is 35.9 cm^{-1}, about 50 times that of the ground state. We may conclude that the motions associated with x_1, x_2 and x_4 do not lead from one equilibrium configuration to the other except by way of a very high potential barrier. This is also a plausible conclusion when the actual motions associated with these coordinates are considered.

Since the subject of our study is the doublet separation and since this depends almost wholly upon x_3 we shall ignore the remaining coordinates. The actual Hamiltonian will be approximated by one which is a function of x_3 alone, the other coordinates being given their equilibrium values, namely zero. The normal coordinate x_3 describes a deformation in which the hydrogen atoms move symmetrically with respect to the axis of the pyramid, and in first approximation the N−H bond distances are unchanged. Thus, whatever the value of x_3, the molecule retains its axial symmetry. The moments of inertia are of course functions of x_3 but the products of inertia are always zero. Under these assumptions, the Hamiltonian takes on a very simple form. We express it in terms of y rather than of x_3 where y is the actual displacement of each hydrogen relative to the nitrogen atom, taken, however, along the path of the normal coordinate x_3.

$$H=(P_\alpha^2+P_\beta^2)/2I_A+P_\gamma^2/2I_C+p^2/2\mu+V.$$

P_α, P_β and P_γ are the components of the total angular momentum of the system. The combinations occurring here may be diagonalized at once leading to a Hamiltonian which contains only the vibrational coordinate y and its conjugate momentum p.

$$H=p^2/2\mu+V+\hbar^2(J^2+J-K^2)/2I_A+\hbar^2K^2/2I_C.$$

It will prove convenient to rearrange the terms in the Hamiltonian; let,

$$H=p^2/2\mu+V+\delta V+W_R^0,$$

where W_R^0 is a constant equal to $A_e(J^2+J-K^2)+C_eK^2$ and

$$\delta V=\hbar^2(J^2+J-K^2)(1/2I_A-1/2I_A^0)+\hbar^2K^2(1/2I_C-1/2I_C^0).$$

The problem has now been brought to such a form that it differs from the usual double minimum problem in only two respects, (1) the potential is increased by δV and (2) the energy constant of the whole system is increased by W_R^0. This last point will, of course, have no effect upon the quantity to be calculated, namely the splitting of the levels caused by the double minimum potential.

This splitting has been calculated by Dennison and Uhlenbeck[10] using the W-K-B approximation.

They find

$$\Delta=2\hbar\nu/A^2,$$

where

$$A^2=\exp\left[(2/\hbar)\int_0^{y_1}[2\mu(V-E)]^{\frac{1}{2}}dy\right].$$

The origin for the coordinate y is chosen to be the equatorial plane through the nitrogen atom, that is, at the center of the barrier separating the two equilibrium positions for the hydrogens. y_1 is the first root of $V-E=0$.

In the present calculation V must be increased by δV and E by δE, the latter to take account of

TABLE IV. *Values of constants.*

J	K	$C_1^0-C_0^0-A_1^0+A_0^0$	J	K	$C_1^0-C_0^0-A_1^0+A_0^0$
6→5	4	−0.300	10→9	7	−0.020
	3	−0.213		8	−0.024
	2	−0.266	9→8	7	−0.016
	1	−0.240		6	−0.024
5→4	3	−0.273			
	2	−0.256		Average	−0.021
	1	−0.243			
4→3	2	−0.270			
	1	−0.251			
3→2	1	−0.266			
5→6	3	−0.258			
3→4	1	−0.210			
	Average	−0.254			

[10] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932).

the fact that the average of the levels s and a may be slightly shifted by δV. A^2 can be developed since δV is small. Thus $\Delta+\delta\Delta=2\hbar\nu/A^2$ and

$$A^2=\exp\left[(2/\hbar)\int_0^{y_1+\delta y_1}[2\mu(V+\delta V-E-\delta E]^{\frac{1}{2}}dy\right]$$

$$=\exp(2/\hbar)\left[\int_0^{y_1}[2\mu(V-E)]^{\frac{1}{2}}dy + \int_0^{y_1}\mu(\delta V-\delta E)[2\mu(V-E)]^{-\frac{1}{2}}dy + \tfrac{1}{2}[2\mu(\delta V-\delta E)]^{\frac{1}{2}}_{y=y_1}\delta y_1\right].$$

The first term in this exponent gives Δ while the next two determine $\delta\Delta$. The third term may be expected to be negligible in comparison with the second since the integrand is so small in the region y_1 to $y_1+\delta y_1$. A numerical calculation indicates that it contributes less than one percent to $\delta\Delta$ and consequently we shall ignore it. If we assume that $\delta\Delta$ is small, the exponential may be developed[11] and we obtain,

$$\delta\Delta=-(2\Delta/\hbar)\int_0^{y_1}\mu(\delta V-\delta E)[2\mu(V-E)]^{-\frac{1}{2}}dy.$$

It does not appear to be possible to evaluate this integral by any means other than numerical quadrature. We have chosen to use for V the double minimum potential proposed by Manning.[12]

$$V/hc=a\,\mathrm{sech}^4(y/2\rho)-b\,\mathrm{sech}^2(y/2\rho).$$

This function has the correct general form but there is no reason to suppose that it is the best function for describing the ammonia molecule. However, it is well known that the splitting of the levels is rather independent of the particular form of the potential. The constants obtained by Manning from the data for ammonia are $a=66{,}551$, $b=109{,}619$ and $\rho=0.04793(\hbar/c\mu)^{\frac{1}{2}}$. The mean energies E are not given directly by Manning but only the energy differences. A calculation yields as the value for the first excited state $(E_1^s+E_1^a)/2hc=-43{,}692.0$.

The quantity δV may be found by writing out the moments of inertia I_A and I_C. These will be expressed first as functions of two variables, r, the distance between a hydrogen and the nitrogen atom, and α, the angle between a N−H bond and the equatorial plane through the nitrogen.

$$I_A=[3mM/(3m+M)]r^2\sin^2\alpha+\tfrac{3}{2}mr^2\cos^2\alpha,$$
$$I_C=3mr^2\cos^2\alpha.$$

The motion corresponding to the frequency ν_3 is, to a high degree of approximation, one in which r remains constant and α alone varies. The relationship between α and y is then, $\alpha=\alpha_0 y/y_0$ where y_0 is the distance along the arc from the equatorial plane to the equilibrium position and α_0 is the equilibrium value of the angle. From previous work[1] these are known to be, 0.386×10^{-8} cm and 21° 49.7′, respectively. Actually the assumption that r is a constant is not quite justified and will be modified later. It is very instructive, however, to carry out the computation under this assumption and that will be done first. δV is then determined as a function of y and the only quantity not yet discussed is δE. δE is the change in the average position of the levels s and a caused by the rotation. Since this change, for example the term $\frac{1}{2}(A_V^s+A_V^a)-A_e$, is proportional to $V+\frac{1}{2}$, it is evident that for the first excited state,

$$\delta E/hc=\tfrac{3}{2}[\tfrac{1}{2}(A_1^s+A_1^a)-\tfrac{1}{2}(A_0^s+A_0^a)]\times(J^2+J-K^2)+\tfrac{3}{2}[\tfrac{1}{2}(C_1^s+C_1^a)-\tfrac{1}{2}(C_0^s+C_0^a)]K^2.$$

Introducing the observed values we obtain,

$$\delta E/hc=0.05(J^2+J-K^2)-0.16K^2.$$

The contribution due to δE turns out to be $\delta\Delta/hc=0.007(J^2+J)-0.029K^2$, which is considerably smaller than that due to δV.

The numerical evaluation of the integral determining $\delta\Delta$ for the first excited state is not difficult. Near the point $y=y_1$ the integrand becomes infinite but this portion could be ob-

[11] The approximation of developing the exponential is only justified as long as the integral occurring in the exponent is small compared with unity. A substitution of the numerical values to be obtained later shows that this is true for the lines actually used in the analysis. For lines of large ordinal numbers where the multiplet spacings are correspondingly large, this will no longer be the case and it is probable that the energy levels cannot be expressed in the form of Eq. (1).

[12] M. F. Manning, J. Chem. Phys. 3, 136 (1935).

tained through an exact integration where, however, the potential was approximated by a straight line. Multiplying the integral by the observed splitting in the absence of rotational interaction, namely $\Delta/hc=35.8$ we find,

$$\delta\Delta/hc=-0.105(J^2+J)+0.194K^2.$$

It will be recalled that the observed change of splitting is

$$(\delta\Delta/hc)_{\text{obs}}=-0.17(J^2+J)+0.23K^2.$$

Clearly this first theoretical estimate of $\delta\Delta$ is only moderately satisfactory. It was based upon the assumption that the distance r between each hydrogen and the nitrogen atom remains constant throughout the motion. This point may now be reexamined. The normal coordinate treatment of the problem yields not only the frequencies but also the motion associated with each frequency. Thus it is easy to show from the normal frequency determinant that, in the motion ν_3, the hydrogen atoms oscillate along lines which make an angle β_0 with the symmetry axis of the pyramid where

$$\cot\beta_0=\sqrt{3}(m\lambda_3-b)/c.$$

The quantities b and c are potential constants the latest values of which are given in reference 1. A substitution yields $\beta_0=16°\,7.2'$. The lines along which the hydrogens would travel under the assumption that r remains constant are easily found from the known equilibrium configuration of the ammonia molecule. These lines make an angle $\alpha_0=21°\,49.7'$ with the axis of the pyramid.

Thus as the hydrogen atoms move toward the equatorial plane through the nitrogen, the distance r *decreases* and at such a rate that the angle between the line along which they move and the line perpendicular to the N−H bond is $\alpha_0-\beta_0=5°\,42.5'=0.10$ radian. If this motion were to continue from the equilibrium position all the way to the equatorial plane r should be set equal to

$$r_0[1-0.10(\alpha_0-\alpha)]\leqq r_0[1-0.10\alpha_0(1-y/y_0)].$$

This last approximation depends upon the fact that the distance along the actual path is very nearly equal to the distance along the arc for such a small angle $\alpha_0-\beta_0$.

The spiral path postulated for the hydrogen particles has one unsatisfactory feature, namely that it makes an inward cusp at the equatorial plane. This may be eliminated by adding a further term to the expression for r; let,

$$r=r_0[1-0.10(\alpha_0-\alpha)+(0.05/\alpha_0)(\alpha_0-\alpha)^2]$$
$$\leqq r_0[1-0.05\alpha_0+0.05\alpha_0(y/y_0)^2].$$

This function satisfies the condition imposed by the normal coordinate treatment, namely $(dr/d\alpha)_{\alpha=\alpha_0}=0.10$, and has no cusp at the equatorial plane since $(dr/d\alpha)_{\alpha=0}=0$. We are well aware that very little reliance can be placed upon this estimate for r. It must be emphasized that the normal coordinate treatment can only give information concerning the displacements near the equilibrium configuration. Our function contains this information and is otherwise merely plausible.

The integral determining $\delta\Delta$ may now be recomputed. It yields the result,

$$(\delta\Delta/hc)_{\text{theo}}=-0.162(J^2+J)+0.222K^2.$$

The agreement between $(\delta\Delta)_{\text{theo}}$ and $(\delta\Delta)_{\text{obs}}$ is almost perfect and some remarks should be made concerning its significance. The change in the splitting of the levels is an effect which depends upon the potential energy function of the molecule at some distance from the equilibrium configuration, namely in the region near the potential barrier. From the motion near the equilibrium configuration we have estimated the manner in which the molecule most easily passes from one equilibrium position to the other, that is, we have estimated the distance r as a function of α. This estimate was admittedly very rough but the fact that it leads to a correct value of $\delta\Delta$, indicates that it must be of the correct order of magnitude.

The agreement may be interpreted as furnishing information on the trustworthiness of the potential constants which have been used. It will be recalled that these were obtained[1] from estimates of the normal frequencies of the ammonia molecule and not, as in the usual procedure, from the positions of the fundamental bands. This latter method was employed by Slawsky and Dennison and led to rather different values for the constants. A substitution of the older con-

stants yields the angle $\beta_0 = 28° 40'$ and thus would predict that as the hydrogens approach the equatorial plane, the distance r *increases*. This result would have destroyed the agreement between the calculated and observed separation of the double minimum levels. One further point may be noted. If the potential of the ammonia molecule was of the valence type and contained no cross product term between the change in the valence angles and the change in valence distance, the angle β_0 may be computed readily and is $22° 1'$. This also predicts an increase of r, although only a slight one, as the hydrogens approach the plane and consequently would not lead to the very satisfactory agreement which we have obtained.

The change in the splitting of the ground level may be calculated in a similar fashion. It will be considerably smaller, partly because the integral is smaller but principally because the splitting itself $\Delta_0/hc = 0.66$ is so small. We find

$$A_0^a - A_0^s = -0.0011,$$
$$C_0^a - C_0^s = 0.0005.$$

The first of these values was determined experimentally and found to be $A_0^a - A_0^s = -0.00_5$. The agreement is satisfactory although not very significant.

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The Vibration-Rotation Energies of Polyatomic Molecules

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The quantum-mechanical Hamiltonian function, H, for the general vibrating-rotating polyatomic molecule of N atoms has been expanded by the method of Wilson and Howard to second order of approximation. It has been practicable to obtain solutions of the Schrödinger equation $(H-E)\psi = 0$ for asymmetric molecules, axially symmetric molecules and linear molecules. Expressions for the anharmonic terms occurring in the vibration energy, the effective moments of inertia, the amplitudes of the internal angular momentum of oscillation and the centrifugal distortion coefficients are derived so that when the normal coordinates are known the vibration-rotation energies of a polyatomic molecule may be calculated from the results given. Tetrahedrally symmetric molecules and models in which internal rotation occurs are regarded as anomalous cases and are not treated.

I. INTRODUCTION

RECENTLY a number of papers have appeared in which the form of the vibration-rotation energies of certain polyatomic molecular models[1] have been derived to a second order of approximation. The method followed has in each instance been equivalent to that delineated by Wilson and Howard,[2] although the details have varied slightly from case to case. The method consists essentially in approximating by the method of the perturbation theory to three items, namely: the energy of the atomic nuclei oscillating anharmonically about their positions of equilibrium in a set of body-fixed coordinates; the effective moments of inertia of the molecule regarded as a semi-rigid rotator and the distortion of the molecular energies due to the centrifugal forces.

An inspection of the final results in these papers reveals that they are nearly always of the same form. Thus, for example, the oscillational energy always consists of a set of terms linear in the

[1] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933); W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939); W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. **56**, 895 (1939); W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. **56**, 1051 (1939); B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940); Ta-You Wu, J. Chem. Phys. **8**, 489 (1940); S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941); W. H. Shaffer, J. Chem. Phys. **9**, 607 (1941); W. H. Shaffer and A. H. Nielsen, J. Chem. Phys. **9**, 847 (1941).
[2] E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 262 (1936).

vibration quantum numbers, the coefficients of which are the normal frequencies; a set of terms quadratic in the vibration quantum numbers, the coefficients of which depend in a complicated fashion on the normal frequencies, the non-vanishing constants occurring in the cubic and quartic parts of the potential energy function and upon the dimensions of the molecule. Also the effective moments of inertia are in each case linear functions of the vibration quantum numbers and depend in an involved manner upon the size and the shape of the molecule, the normal frequencies and the coefficients of the anharmonic part of the potential energy which is cubic in the coordinates. The coefficients of the centrifugal distortion are to second order of approximation always independent of the quantum numbers and depend only upon the normal frequencies and the dimensions of the model. One may summarize this by stating that to a second order of approximation the vibration-rotation energies of a molecule depend always only upon the following items: the normal frequencies, the size and shape of the molecule and the non-vanishing coefficients of the anharmonic terms in the potential energy cubic and quartic in the normal coordinates.

This suggests that it should be practicable to set up and solve the problem of the vibration-rotation energies of a perfectly general molecule of N atoms oscillating and rotating in space. Precisely as before the final formulation should consist of three parts; the vibration energy, the energy of a semi-rigid rotator and the energy due to the distortion of the molecule by the centrifugal forces. To obtain the energies in a particular case it would then be necessary only to solve the problem of the normal frequencies and determine from the symmetry of the model which of the coefficients of the anharmonic terms in the potential energy function are non-vanishing and then insert these results into the general formulation.

We have undertaken to do this and have found that the problem of determining the vibration-rotation energies of the general molecule is in reality much simpler to carry out in detail than that of the special cases. In the following sections we shall set down the results of this investigation. It will be found that it is far less time consuming to arrive at the vibration-rotation energies of a particular molecule by the general method than it is to derive them independently for a particular model.

II. The Quantum-Mechanical Hamiltonian

The problem of determining the vibration-rotation energies of a polyatomic molecule reduces to that of finding the solutions and the eigenvalues of the quantum-mechanical equation

$$(H-E)\psi=0, \tag{1}$$

characteristic of the motion in space of the molecule.

In discussing the motion of a molecule it is convenient to make use of a set of coordinates x, y and z fixed in the molecule and a set of space fixed coordinates x', y' and z'. The origin of the two sets of coordinates shall be the same and they shall be related to each other by the Eulerian angles θ, φ and ψ, defined as follows: θ is the angle between the fixed z' axis and the axis z; φ, the angle between the x axis and the nodal line and ψ the angle between the nodal line and the x' axis. The general polyatomic molecule will contain N atomic nuclei all of which may have different masses. The kinetic energy of these nuclei when expressed in terms of the coordinates x', y' and z' fixed in space will be

$$T=\tfrac{1}{2}\sum_{i=1}^{i=N} M_i(\dot{x}_i'^2+\dot{y}_i'^2+\dot{z}_i'^2). \tag{2}$$

The molecule is so oriented in the coordinates x, y, and z that the equilibrium position of the ith particle will be x_i^0, y_i^0 and z_i^0 subject to the restrictions:

$$\sum_{i=1}^{i=N} M_i x_i^0=0, \quad \sum_{i=1}^{i=N} M_i y_i^0=0, \quad \sum_{i=1}^{i=N} M_i z_i^0=0 \tag{3a}$$

and

$$\sum_{i=1}^{i=N} M_i x_i^0 y_i^0=0, \quad \sum_{i=1}^{i=N} M_i x_i^0 z_i^0=0, \quad \sum_{i=1}^{i=N} M_i y_i^0 z_i^0=0. \tag{3b}$$

The first condition states that the center of gravity of the molecule coincides with the origin of the coordinates x, y, z when the atomic nuclei are in their equilibrium positions. The second condition states that the axes x, y, and z coincide with the principal axes of inertia of the molecule. The actual positions in the body fixed axes of the ith particle will be designated by x_i, y_i and z_i where $x_i=\overset{0}{x_i}+\delta x_i$, $y_i=\overset{0}{y_i}+\delta y_i$, etc., δx_i, δy_i and δz_i being the displacements of the ith nucleus from its position of equilibrium. Expressed in these coordinates the kinetic energy may be written:

$$2T=\sum_{i=1}^{i=N} M_i(\dot{x}_i^2+\dot{y}_i^2+\dot{z}_i^2)+\sum_{\alpha=x,\,y,\,z}[I_{\alpha\alpha}\overset{2}{\omega}_\alpha-\sum_{\beta=x,\,y,\,z}{}' I_{\alpha\beta}\omega_\alpha\omega_\beta]+2\sum_\alpha \Omega_\alpha\omega_\alpha, \tag{4}$$

where $I_{\alpha\alpha}$ are the instantaneous moments of inertia[3] $\sum_{i=1}^{i=N} M_i(\beta_i^2+\gamma_i^2)$ and $I_{\alpha\beta}$ are the instantaneous products of inertia which by virtue of Eq. (3b) become equal to $\sum_{i=1}^{i=N} M_i(\overset{0}{\beta_i}\delta\alpha_i+\overset{0}{\alpha_i}\delta\beta_i+\delta\alpha_i\delta\beta_i)$. In Eq. (4) ω_α are the components of the angular velocity along the x, y and z axes[4] and Ω_α take the form:

$$\Omega_\alpha=\sum_{i=1}^{i=N} M_i(\dot{\gamma}_i\delta\beta_i-\dot{\beta}_i\delta\gamma_i).$$

The first set of terms in (4) represents the kinetic energy of the atomic nuclei oscillating about their positions of equilibrium in the force field of the electrons. The form of this force field will depend upon the nature of the assumptions made concerning it. For our purpose we shall take for the quadratic part of the potential energy a function which may be regarded as perfectly general in the coordinates:

$$V_0=\tfrac{1}{2}\sum K_{ij,\,mn}\delta s_{ij}\delta s_{mn}, \tag{5}$$

where $K_{ij,\,mn}$ may be regarded as force constants and the δs_{ij} is the variation of the distance between the atomic nuclei i and j. The displacements δs_{ij} can be expressed in terms of the coordinates x_i, y_i and z_i so that (5) becomes:

$$V_0(\delta s_{ij})=V_0(x_i,\,y_i,\,z_i). \tag{6}$$

The coordinates x_i, y_i and z_i which occur in (4) and (6) are not all independent of each other, but are subject to the restrictions:

$$\sum_{i=1}^{i=N} M_i\alpha_i=0\ (\alpha \text{ taking the values } x,\ y \text{ and } z), \tag{7}$$

$$\sum_{i=1}^{i=N} M_i(\overset{0}{\alpha_i}\delta\beta_i-\overset{0}{\beta_i}\delta\alpha_i)=0\ (\alpha \text{ and } \beta \text{ taking the values } x,\ y \text{ and } z \text{ but } \alpha\neq\beta), \tag{8}$$

the first of which states that the center of gravity of the molecule remains at rest in these coordinates and the second of which stipulates that to zero order of approximation the internal angular momentum is equal to zero. With the aid of (7) and (8) it is possible to determine the normal coordinates of the system.[5] Of these there will be $3N-6$, one normal coordinate, Q_s', for each normal frequency ω_s. Not infrequently, however, a molecule will have so high a degree of symmetry that in certain of its modes it will be oscillating in force fields which are isotropic in two or three dimensions. In such cases two- and threefold vibrational degeneracies will arise, i.e., there will be

[3] Certain molecular spectroscopists [see for example R. S. Mulliken, Phys. Rev. **59**, 873 (1941)] have found it convenient to designate the moments of inertia of the molecule in ascending order of magnitude by I_a, I_b and I_c. In a discussion of the vibration-rotation energies of a general polyatomic molecule it is inconvenient to assign definitely any one of the moments of inertia as the largest or the smallest. In this work the z axis will be taken as the approximately unique axis of the rotator. In some cases (for example, the methyl halide molecules or the formaldehyde molecule) I_{zz} will therefore be the smallest moment of inertia, i.e., I_a; in other cases (for example, the BF_3 molecule or the H_2Se molecule) I_{zz} will be the largest moment of inertia, i.e., I_c. It is probably always convenient to identify the moment of inertia I_{yy} with I_b.

[4] Explicit expressions for ω_α may be found in books dealing with classical mechanics.

[5] See, for example, E. T. Whittaker, *Analytical Dynamics*, fourth edition, p. 177.

respectively, two and three coordinates Q' associated with the same frequency ω. It is convenient, for this reason, to denote a normal coordinate by $Q'_{s\sigma}$ rather than simply by Q'_s, where s will denote the particular frequency to be associated with the coordinate and σ will take the values 1; 1, 2 and 1, 2, 3 depending upon whether the frequency is non-degenerate, two- or threefold degenerate, respectively. Thus, for example, the non-degenerate frequency of a harmonic oscillator oscillating with a frequency ω_a will have associated with it the coordinate $Q'_{a,1}$, while the twofold degenerate frequency of a two-dimensionally isotropic oscillator oscillating with a frequency ω_b will have associated with it the two coordinates $Q'_{b,1}$ and $Q'_{b,2}$, etc.

It is always possible to express the δx_i, δy_i and δz_i in terms of the normal coordinates $Q'_{s\sigma}$ as follows:

$$\delta x_i=\sum l'_{is\sigma}Q'_{s\sigma}, \quad \delta y_i=\sum m'_{is\sigma}Q'_{s\sigma}, \quad \delta z_i=\sum n'_{is\sigma}Q'_{s\sigma}, \tag{9}$$

so that when these are substituted into the first term of (4) and into (6) we obtain for the kinetic and potential energies of the oscillational motion the following relations:

$$2T=\sum \mu_{s\sigma}\dot{Q}'^2_{s\sigma}, \quad 2V_0=\sum k_s Q'^2_{s\sigma}, \tag{10}$$

where the $\mu_{s\sigma}$ are the reduced masses and k_s are the generalized forces constants, equal, respectively, to $4\pi^2c^2\mu_s\omega_s^2$, which will be complicated relations of the $K_{ij,mn}$. It is convenient to replace the coordinates $Q'_{s\sigma}$ by $(\mu_{s\sigma})^{-\frac{1}{2}}Q_{s\sigma}$ so that instead of (10) we shall have:

$$2T=\sum_{s,\sigma}\dot{Q}^2_{s\sigma} \quad \text{and} \quad 2V_0=\sum_{s,\sigma}\lambda_s Q^2_{s\sigma} \ (\lambda_s=(2\pi c\omega_s)^2). \tag{10'}$$

Evidently then

$$\delta x_i=\sum_{s,\sigma} l_{is\sigma}Q_{s\sigma}, \quad \delta y_i=\sum_{s,\sigma} M_{is\sigma}Q_{s\sigma}, \quad \delta z_i=\sum_{s,\sigma} n_{is\sigma}Q_{s\sigma} \tag{9'}$$

where $l_{is\sigma}=(\mu_{s\sigma})^{-\frac{1}{2}}l'_{is\sigma}$, etc.

In terms of the coordinates $Q_{s\sigma}$ the expressions for the cubic and the quartic terms in the potential energy expansion may conveniently be taken to be:

$$\begin{aligned} V_1&=\sum_{s,\sigma}\sum_{s',\sigma'}\sum_{s'',\sigma''} k_{ss's''}Q_{s\sigma}Q_{s'\sigma'}Q_{s''\sigma''}, \quad (s\leqslant s'\leqslant s''),\\ V_2&=\sum_{s,\sigma}\sum_{s',\sigma'}\sum_{s'',\sigma''}\sum_{s''',\sigma'''} k_{ss's''s'''}Q_{s\sigma}Q_{s'\sigma'}Q_{s''\sigma''}Q_{s'''\sigma'''}. \quad (s\leqslant s'\leqslant s''\leqslant s'''). \end{aligned} \tag{11}$$

The appropriate Hamiltonian form for the kinetic energy of the general molecule in the quantum mechanics will, according to Wilson and Howard,[6] be the following:

$$T=\tfrac{1}{2}\sum_{\alpha,\beta}\mu_{\alpha\beta}P_\alpha P_\beta-\sum_\alpha h_\alpha P_\alpha+\tfrac{1}{2}\sum_{\alpha,\beta}\mu^{\frac{1}{2}}p_\alpha\mu_{\alpha\beta}\mu^{-\frac{1}{2}}p_\beta+\tfrac{1}{2}\sum_{s,\sigma}\mu^{\frac{1}{2}}p_{s,\sigma}\mu^{-\frac{1}{2}}p_{s,\sigma}, \tag{12}$$

where $h_\alpha=\frac{1}{2}\sum_\beta\{2\mu_{\alpha\beta}p_\beta+(p_\beta\mu_{\alpha\beta})+\mu_{\alpha\beta}\mu^{\frac{1}{2}}(p_\beta\mu^{-\frac{1}{2}})\}$ and α, β are summed over x, y and z. In Eq. (12),

$$\mu_{\alpha\alpha}=(I'_{\beta\beta}I'_{\gamma\gamma}-I'^2_{\beta\gamma})/\Delta \quad \text{and} \quad \mu_{\alpha\beta}=\mu_{\beta\alpha}=(I'_{\gamma\gamma}I'_{\alpha\beta}-I'_{\alpha\gamma}I'_{\beta\gamma})/\Delta, \tag{13}$$

where $I'_{\alpha\beta}$ are respectively defined in the following manner:

$$\begin{aligned} I'_{xx}&=I_{xx}-\sum_{s'\sigma'}\mathfrak{X}^2_{s'\sigma'}, \qquad I'_{yy}=I_{yy}-\sum_{s'\sigma'}\mathfrak{Y}^2_{s'\sigma'}, \qquad I'_{zz}=I_{zz}-\sum_{s'\sigma'}\mathfrak{Z}^2_{s'\sigma'},\\ I'_{xy}&=I_{xy}+\sum_{s'\sigma'}\mathfrak{X}_{s'\sigma'}\mathfrak{Y}_{s'\sigma'}, \quad I'_{xz}=I_{xz}+\sum_{s'\sigma'}\mathfrak{X}_{s'\sigma'}\mathfrak{Z}_{s'\sigma'}, \quad I'_{yz}=I_{yz}+\sum_{s'\sigma'}\mathfrak{Y}_{s'\sigma'}\mathfrak{Z}_{s'\sigma'} \end{aligned} \tag{14}$$

in which

$$\begin{aligned} \mathfrak{X}_{s'\sigma'}&=\sum_i\sum_{s,\sigma}M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})Q_{s\sigma},\\ \mathfrak{Y}_{s'\sigma'}&=\sum_i\sum_{s,\sigma}M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma'}l_{is\sigma})Q_{s\sigma},\\ \mathfrak{Z}_{s'\sigma'}&=\sum_i\sum_{s,\sigma}M_i(l_{is\sigma}m_{is'\sigma'}-l_{is'\sigma'}m_{is\sigma})Q_{s\sigma}, \end{aligned}$$

[6] Darling and Dennison have given a form which is slightly different from that derived by Wilson and Howard. To second order of approximation, however, they are entirely equivalent.

and where

$$\Delta=\begin{vmatrix} I'_{xx} & -I'_{xy} & -I'_{xz} \\ -I'_{xy} & I'_{yy} & -I'_{yz} \\ -I'_{xz} & -I'_{yz} & I'_{zz} \end{vmatrix}=\mu^{-1}.$$

Explicitly the quantities I'_{xx}, I'_{yy}, etc., will become:

$$I'_{xx}=I^{(e)}_{xx}+\sum_{s,\sigma} a_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} A_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},$$

$$I'_{yy}=I^{(e)}_{yy}+\sum_{s,\sigma} b_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} B_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},$$

$$I'_{zz}=I^{(e)}_{zz}+\sum_{s,\sigma} c_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} C_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''}.$$

$$I'_{xy}=\sum_{s\sigma} d_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} D_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},$$

$$I'_{xz}=\sum_{s\sigma} e_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} E_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},$$

$$I'_{yz}=\sum_{s\sigma} f_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} F_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},$$

where

$$a_{s\sigma}=2\sum_i M_i(y^0_i m_{is\sigma}+z^0_i n_{is\sigma});\quad b_{s\sigma}=2\sum_i M_i(z^0_i n_{is\sigma}+x^0_i l_{is\sigma}),$$

$$c_{s\sigma}=2\sum_i M_i(x^0_i l_{is\sigma}+y^0_i m_{is\sigma});\quad d_{s\sigma}=\sum_i M_i(x^0_i m_{is\sigma}+y^0_i l_{is\sigma}),$$

$$e_{s\sigma}=\sum_i M_i(y^0_i n_{is\sigma}+z^0_i m_{is\sigma});\quad f_{s\sigma}=\sum_i M_i(z^0_i l_{is\sigma}+x^0_i n_{is\sigma}),$$

$$A_{s\sigma s''\sigma''}=\{\sum_i M_i(m_{is\sigma}m_{is''\sigma''}+n_{is\sigma}n_{is''\sigma''})-\sum_{s'\sigma'}[\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})\times\sum_{i''} M_{i''}(m_{i''s''\sigma''}n_{i''s'\sigma'}-m_{i''s'\sigma'}n_{i''s''\sigma''})]\},$$

$$B_{s\sigma s''\sigma''}=\{\sum_i M_i(n_{is\sigma}n_{is''\sigma''}+l_{is\sigma}l_{is''\sigma''})-\sum_{s'\sigma'}[\sum_i M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma}l_{is\sigma})\times\sum_{i''} M_{i''}(n_{i''s''\sigma''}l_{i''s'\sigma'}-n_{i''s'\sigma'}l_{i''s''\sigma''})]\},$$

$$C_{s\sigma s''\sigma''}=\{\sum_i M_i(l_{is\sigma}l_{is''\sigma''}+m_{is\sigma}m_{is''\sigma''})-\sum_{s'\sigma'}[\sum_i M_i(l_{is\sigma}m_{is'\sigma'}-l_{is'\sigma}m_{is\sigma})\times\sum_{i''} M_{i''}(l_{i''s''\sigma''}m_{i''s'\sigma'}-l_{i''s'\sigma'}m_{i''s''\sigma''})]\},\tag{15}$$

$$D_{s\sigma s''\sigma''}=\{\sum_i M_i l_{is\sigma}m_{is''\sigma''}+\sum_{s'\sigma'}[\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma}n_{is\sigma})\times\sum_{i''} M_{i''}(n_{i''s''\sigma''}l_{i''s'\sigma'}-n_{i''s'\sigma'}l_{i''s''\sigma''})]\},$$

$$E_{s\sigma s''\sigma''}=\{\sum_i M_i m_{is\sigma}n_{is''\sigma''}+\sum_{s'\sigma'}[\sum_i M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma}l_{is\sigma})\times\sum_{i''} M_{i''}(l_{i''s''\sigma''}m_{i''s'\sigma'}-l_{i''s'\sigma'}m_{i''s''\sigma''})]\},$$

$$F_{s\sigma s''\sigma''}=\{\sum_i M_i n_{is\sigma}l_{is''\sigma''}+\sum_{s'\sigma'}[\sum_i M_i(l_{is\sigma}m_{is'\sigma'}-l_{is'\sigma}m_{is\sigma})\times\sum_{i''} M_{i''}(m_{i''s''\sigma''}n_{i''s'\sigma'}-m_{i''s'\sigma'}n_{i''s''\sigma''})]\}.$$

The quantities P_α are the operators for the three components of the angular momentum referred to the moving coordinate system and they are defined as follows:

$$P_x=(-ih)(\sin\theta)^{\frac{1}{2}}\left[\frac{-\cos\varphi}{\sin\theta}\left(\frac{\partial}{\partial\psi}-\cos\theta\frac{\partial}{\partial\varphi}\right)+\sin\varphi\frac{\partial}{\partial\theta}\right](\sin\theta)^{-\frac{1}{2}},$$

$$P_y=(-ih)(\sin\theta)^{\frac{1}{2}}\left[\frac{\sin\varphi}{\sin\theta}\left(\frac{\partial}{\partial\psi}-\cos\theta\frac{\partial}{\partial\varphi}\right)+\cos\varphi\frac{\partial}{\partial\theta}\right](\sin\theta)^{-\frac{1}{2}}, \tag{16}$$

$$P_z=(-ih)\partial/\partial\varphi,$$

θ, φ and ψ being the Eulerian angles referred to above. The operators p_x, p_y and p_z which occur in (12) are the operators corresponding to the internal angular momentum due to oscillation and their definition will be given at a later point.

It is convenient here to replace the $Q_{s\sigma}$ by $(h^2/\lambda_s)^{\frac{1}{4}}q_{s\sigma}$. After considerable algebraic manipulation it is possible to set down in orders of magnitude the quantum-mechanical Hamiltonian for the general polyatomic molecule. It will be:

$$H_0=(h/2)\sum_{s\sigma}\lambda_s^{\frac{1}{2}}(p_{s\sigma}^2/h^2+q_{s\sigma}^2)+\tfrac{1}{2}(P_x^2/I_{xx}^{(e)}+P_y^2/I_{yy}^{(e)}+P_z^2/I_{zz}^{(e)}), \tag{17a}$$

$$\begin{aligned}H_1=(-h^{\frac{1}{2}}/4)&\sum_{s\sigma}\lambda_s^{\frac{1}{4}}[(a_{s\sigma}/I_{xx}^{(e)})+(b_{s\sigma}/I_{yy}^{(e)})+(c_{s\sigma}/I_{zz}^{(e)})]p_{s\sigma}-(p_xP_x/I_{xx}^{(e)})-(p_yP_y/I_{yy}^{(e)})\\
&-(p_zP_z/I_{zz}^{(e)})+\sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''}(h^6/\lambda_s\lambda_{s'}\lambda_{s''})^{\frac{1}{4}}k_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}-\tfrac{1}{2}\sum_{s\sigma}(h^2/\lambda_s)^{\frac{1}{2}}\{(a_{s\sigma}P_x^2/(I_{xx}^{(e)})^2)\\
&+(b_{s\sigma}P_y^2/(I_{yy}^{(e)})^2)+(c_{s\sigma}P_z^2/(I_{zz}^{(e)})^2)-(d_{s\sigma}(P_xP_y+P_yP_x)/(I_{xx}^{(e)})(I_{yy}^{(e)}))\\
&-(f_{s\sigma}(P_xP_z+P_zP_x)/(I_{xx}^{(e)})(I_{zz}^{(e)}))-(e_{s\sigma}(P_yP_z+P_zP_y)/(I_{yy}^{(e)})(I_{zz}^{(e)}))\}q_{s\sigma},\end{aligned} \tag{17b}$$

$$\begin{aligned}H_2=(-ih/2)&\sum_{s\sigma}\sum_{s'\sigma'}(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}[(A_{ss\sigma s'\sigma'}/I_{xx}^{(e)})+(B_{ss\sigma s'\sigma'}/I_{yy}^{(e)})+(C_{ss\sigma s'\sigma'}/I_{zz}^{(e)})-(3a_{s\sigma}a_{s'\sigma'}/4(I_{xx}^{(e)})^2)\\
&-(3b_{s\sigma}b_{s'\sigma'}/4(I_{yy}^{(e)})^2)-(3c_{s\sigma}c_{s'\sigma'}/4(I_{zz}^{(e)})^2)-((a_{s\sigma}b_{s'\sigma'}+2d_{s\sigma}d_{s'\sigma'})/2(I_{xx}^{(e)})(I_{(yy)}^{e}))\\
&-(a_{s\sigma}c_{s'\sigma'}+2f_{s\sigma}f_{s'\sigma'})/2(I_{xx}^{(e)})(I_{zz}^{(e)}))-((b_{s\sigma}c_{s'\sigma'}+2e_{s\sigma}e_{s'\sigma'})/2(I_{yy}^{(e)})(I_{zz}^{(e)}))]q_{s\sigma}p_{s'\sigma'}\\
&+\tfrac{1}{2}(p_x^2/I_{xx}^{(e)}+p_y^2/I_{yy}^{(e)}+p_z^2/I_{zz}^{(e)})+\sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''}\sum_{s'''\sigma'''}(h^8/\lambda_s\lambda_{s'}\lambda_{s''}\lambda_{s'''})^{\frac{1}{4}}k_{ss's''s'''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}q_{s'''\sigma'''}\\
&-\tfrac{1}{2}\sum_{s\sigma}\sum_{s''\sigma''}(h^4/\lambda_s\lambda_{s''})^{\frac{1}{2}}q_{s\sigma}q_{s''\sigma''}\{(I_{xx}^{(e)})^{-2}[A_{ss\sigma s''\sigma''}-(a_{s\sigma}a_{s''\sigma''}/I_{xx}^{(e)})-(d_{s\sigma}d_{s''\sigma''}/I_{yy}^{(e)})\\
&-(f_{s\sigma}f_{s''\sigma''}/I_{zz}^{(e)})]P_x^2+(I_{yy}^{(e)})^{-2}[B_{ss\sigma s''\sigma''}-(d_{s\sigma}d_{s''\sigma''}/I_{xx}^{(e)})-(b_{s\sigma}b_{s''\sigma''}/I_{yy}^{(e)})\\
&-(e_{s\sigma}e_{s''\sigma''}/I_{zz}^{(e)})]P_y^2+(I_{zz}^{(e)})^{-2}[C_{ss\sigma s''\sigma''}-(f_{s\sigma}f_{s''\sigma''}/I_{xx}^{(e)})-(e_{s\sigma}e_{s''\sigma''}/I_{yy}^{(e)})\\
&-(c_{s\sigma}c_{s''\sigma''}/I_{zz}^{(e)})]P_z^2+[(I_{xx}^{(e)})(I_{yy}^{(e)})]^{-1}[D_{ss\sigma s''\sigma''}-(a_{s\sigma}d_{s''\sigma''}/I_{xx}^{(e)})-(b_{s\sigma}d_{s''\sigma''}/I_{yy}^{(e)})\\
&-(e_{s\sigma}f_{s''\sigma''}/I_{zz}^{(e)})](P_xP_y+P_yP_x)+[(I_{xx}^{(e)})(I_{zz}^{(e)})]^{-1}[F_{ss\sigma s''\sigma''}-(a_{s\sigma}f_{s''\sigma''}/I_{xx}^{(e)})\\
&-(d_{s\sigma}e_{s''\sigma''}/I_{yy}^{(e)})-(c_{s\sigma}e_{s''\sigma''}/I_{zz}^{(e)})](P_xP_z+P_zP_x)+[(I_{yy}^{(e)})(I_{zz}^{(e)})]^{-1}[E_{ss\sigma s''\sigma''}\\
&+(d_{s\sigma}f_{s''\sigma''}/I_{xx}^{(e)})-(e_{s\sigma}f_{s''\sigma''}/I_{yy}^{(e)})-(e_{s\sigma}c_{s''\sigma''}/I_{zz}^{(e)})](P_yP_z+P_zP_y)\}.\end{aligned} \tag{17c}$$

In terms of the coordinates $q_{s\sigma}$ and their conjugate momenta $p_{s\sigma}=-ih(\partial/\partial q_{s\sigma})$ the operators p_α will be the following:

$$p_x=\sum_i \sum_{s\sigma} \sum_{s''\sigma''} M_i m_{is\sigma} n_{is'\sigma'}[(\lambda_{s'}/\lambda_s)^{\frac{1}{2}} q_{s\sigma} p_{s'\sigma'}-(\lambda_s/\lambda_{s'})^{\frac{1}{2}} q_{s'\sigma'} p_{s\sigma}], \tag{18}$$

p_y and p_z being obtained from (18) by permuting $l_{is\sigma}$, $m_{is\sigma}$ and $n_{is\sigma}$ in cyclic rotation.

III. The Energy Values of the Molecule

In this section we shall endeavor to obtain the eigenfunctions of the Hamiltonian, H, which was arrived at in Section II. We shall approximate these by resorting to the methods of the perturbation theory of quantum mechanics proceeding after the manner of Shaffer, Nielsen and Thomas[1] in dealing with the vibration-rotation energy levels of the tetrahedrally symmetric XY_4 type of molecule.

This method, recognizing that all terms in H_1 save the Coriolis terms arising from the degenerate oscillations can contribute first in second order of approximation, depends upon the effectiveness of carrying out a contact transformation on H, $THT^{-1}=H_0'+H_1'+H_2'+\cdots$ such that H_1' will to second order contain only the above Coriolis terms. It is possible always to find a linear combination of the zero order wave functions such that the matrix H_1' will contain elements only along the principal diagonal. In effect this reduces the problem of obtaining the second order energies to a first order perturbation calculation where the wave functions required are the stabilized wave functions of H_0', i.e., the linear combinations of the zero-order wave functions which will diagonalize $H_0'+H_1'$.

We shall denote the transformation function $e^{i\lambda s}$ by $T(\lambda)$ which to second order of approximation may be written:

$$T=1+i\lambda S-\tfrac{1}{2}\lambda^2 S^2-\cdots. \tag{19}$$

Transformation of the Hamiltonian $H=H_0+H_1+H_2+\cdots$ in the manner indicated above leads to $THT^{-1}=H'=H_0'+H_1'+H_2'+\cdots$. After equating like powers of λ we obtain:

$$H_0'=H_0, \quad H_1'=H_1-i(H_0S-SH_0), \quad H_2'=H_2+(i/2)[S(H_1+H_1')-(H_1+H_1')S]. \tag{20}$$

The portions of H_1 which it is desired to remove consist of terms each of which is a function of the normal coordinates $q_{s\sigma}$ (or the conjugate momenta $p_{s\sigma}$) multiplied by a coefficient which either is a constant or a function of the operators P_α, for example $aq_{s\sigma}$ or $q_{s\sigma}P_x^2$. Such coefficients as occur in the latter example may also be treated as constants for to second order of approximation the error incurred because of the non-commutability of functions of P_α with H_0 will not contribute to the energy. The complete S function will consist of a sum of terms, each element being so chosen that it will remove a single term in H_1. In orders of magnitude the transformed Hamiltonian H' may be written:

$$H_0'=H_0, \tag{21a}$$

$$H_1'=-\sum_i \sum_r (M_i/I_{zz}^{(e)})(l_{ir1}m_{ir2}-l_{ir2}m_{ir1})(q_{r1}p_{r2}-q_{r2}p_{r1})P_z \tag{21b}$$

where r assumes those values of s for which the frequencies ω_s are twofold degenerate;

$$H_2'=H_2-(ih/32)\sum_{s\sigma}\lambda_s^{\frac{1}{2}}[(a_{s\sigma}/I_{xx}^{(e)})+(b_{s\sigma}/I_{yy}^{(e)})+(c_{s\sigma}/I_{zz}^{(e)})]^2-(1/8)\sum_{s\sigma}\lambda_s^{-1}\{(a_{s\sigma}^2/(I_{xx}^{(e)})^4)P_x^4$$
$$+(b_{s\sigma}^2/(I_{yy}^{(e)})^4)P_y^4+(c_{s\sigma}^2/(I_{zz}^{(e)})^4)P_z^4+[(a_{s\sigma}b_{s\sigma}+d_{s\sigma}^2)/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2](P_x^2P_y^2+P_y^2P_x^2)$$
$$+[(a_{s\sigma}c_{s\sigma}+f_{s\sigma}^2)/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2](P_x^2P_z^2+P_z^2P_x^2)+[(b_{s\sigma}c_{s\sigma}+e_{s\sigma}^2)/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2](P_y^2P_z^2+P_z^2P_y^2)\}$$
$$+\tfrac{1}{2}\sum_{s\sigma}\sum_{s'\sigma'}{}'(h/\lambda_s^{\frac{1}{2}}(I_{xx}^{(e)})^2)[(3a_{s\sigma}k_{sss}/\lambda_s)+(a_{s'\sigma'}k_{s's\sigma}/\lambda_{s'})+\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})$$
$$\times\sum_{i'}M_{i'}(m_{i's\sigma}n_{i's'\sigma'}-m_{i's'\sigma'}n_{i's\sigma})(3\lambda_s+\lambda_{s'})/(\lambda_s-\lambda_{s'})]q_{s\sigma}^2P_x^2+\tfrac{1}{2}\sum_{s\sigma}\sum_{s'\sigma'}{}'(h/\lambda_s^{\frac{1}{2}}(I_{yy}^{(e)})^2)$$
$$\times[(3b_{s\sigma}k_{sss}/\lambda_s)+(b_{s'\sigma'}k_{s's\sigma}/\lambda_{s'})+\sum_i M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma'}l_{is\sigma})\sum_{i'}M_{i'}(n_{i's\sigma}l_{i's'\sigma'}-n_{i's'\sigma'}l_{i's\sigma})$$
$$\times(3\lambda_s+\lambda_{s'})/(\lambda_s-\lambda_{s'})]q_{s\sigma}^2P_y^2+\tfrac{1}{2}\sum_{s\sigma}\sum_{s'\sigma'}{}'(h/\lambda_s^{\frac{1}{2}}(I_{zz}^{(e)})^2)[(3c_{s\sigma}k_{sss}/\lambda_s)+(c_{s'\sigma'}k_{s's\sigma}/\lambda_{s'})$$
$$+\sum_i M_i(l_{is\sigma}m_{is'\sigma'}-l_{is'\sigma'}m_{is\sigma})\sum_{i'}M_{i'}(l_{i's\sigma}m_{i's'\sigma'}-l_{i's'\sigma'}m_{i's\sigma})(3\lambda_s+\lambda_{s'})/(\lambda_s-\lambda_{s'})]q_{s\sigma}^2P_z^2$$
$$-\sum_{s\sigma}(h/\lambda_s)^2(3p_{s\sigma}^2q_{s\sigma}^2/h^2+1+3q_{s\sigma}^4/2)-3\sum_{s\sigma}\sum_{s'\sigma'}(h^2/\lambda_s\lambda_{s'})k_{sss}k_{ss's'}q_{s\sigma}^2q_{s'\sigma'}^2$$
$$-\tfrac{1}{2}\sum_{s\sigma}\sum_{s'\sigma'}{}'\sum_{s''\sigma''}{}''(h^2/\lambda_s^{\frac{1}{2}}\lambda_{s'}\lambda_{s''}^{\frac{1}{2}})k_{sss'}k_{s's''s''}q_{s''\sigma''}^2q_{s\sigma}^2-\tfrac{1}{2}\sum_{s\sigma}\sum_{s'\sigma'}{}'(h^2/\lambda_s\lambda_{s'})k_{sss'}^2$$
$$\times\{(2\lambda_s-\lambda_{s'})q_{s\sigma}^4+4\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}q_{s\sigma}^2q_{s'\sigma'}^2+2\lambda_sq_{s\sigma}^2p_{s\sigma}^2/h^2\}/(4\lambda_s-\lambda_{s'})-(i/2)\sum_{s\sigma}\sum_{s'\sigma'}{}'\sum_{s''\sigma''}{}''(h^4/\lambda_s\lambda_{s'}\lambda_{s''})^{\frac{1}{2}}$$
$$\times k_{ss's''}^2\{(2\lambda_s\lambda_{s'}\lambda_{s''}/h^2)[p_{s\sigma}q_{s\sigma}p_{s'\sigma'}q_{s'\sigma'}p_{s''\sigma''}q_{s''\sigma''}-q_{s\sigma}p_{s\sigma}q_{s'\sigma'}p_{s'\sigma'}q_{s''\sigma''}p_{s''\sigma''}]$$
$$+(ih)[\lambda_s^{\frac{1}{2}}(\lambda_s-\lambda_{s'}-\lambda_{s''})q_{s'\sigma'}^2q_{s''\sigma''}^2+\lambda_{s'}^{\frac{1}{2}}(\lambda_{s'}-\lambda_{s''}-\lambda_s)q_{s\sigma}^2q_{s''\sigma''}^2+\lambda_{s''}^{\frac{1}{2}}(\lambda_{s''}-\lambda_s-\lambda_{s'})q_{s\sigma}^2q_{s'\sigma'}^2]\}$$
$$\times h^{-2}\{(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})\}^{-1}+\bar{H},$$

where $\bar{H}$ contains terms which can contribute in higher approximations only. A prime after a summation sign indicates that the indices can here not assume the same values as those which precede them; a double prime following a summation sign preceded by a summation sign with a single prime indicates that the third set of indices do not take the same values as the first two sets and that the second set do not take the values of the first set.

Since the Hamiltonian is entirely general it is possible in principle to proceed to find the eigenvalues for any model in which there may be non-degenerate, twofold degenerate and even threefold degenerate oscillations. In practice, however, it seems advisable to exclude the latter class of molecules from this discussion because the stabilized wave functions in such cases are quite complicated to work with. Such molecules together with molecules in which internal rotation takes place or where other anomalies occur had better be treated as special cases.

In the case of molecules where there are oscillations isotropic only in two dimensions there will be two coordinates q_{a1} and q_{a2} associated with a normal frequency ω_a. It has proved convenient when dealing with such oscillations to introduce the cylindrical polar coordinates ρ_a and χ_a so that $q_{a1}=\rho_a\sin\chi_a$ and $q_{a2}=\rho_a\cos\chi_a$. When this is done the zero- and first-order Hamiltonian operators become:

$$H_0=(h/2)\sum_s\lambda_s^{\frac{1}{2}}(p_s^2/h^2+q_s^2)+\sum_r\lambda_r[(-\partial^2/\partial\rho_r^2)-\rho_r^{-1}(\partial/\partial\rho_r)-\rho_r^{-2}(\partial^2/\partial\chi_r^2)+\rho_r^2]$$
$$+\tfrac{1}{2}[(P_x^2/I_{xx}^{(e)})+(P_y^2/I_{yy}^{(e)})+(P_z^2/I_{zz}^{(e)})], \quad (22a)$$

$$H_1' = \hbar^2 \sum_r (\zeta_r / I_{zz}^{(e)})(\partial^2/\partial\chi_r \partial\varphi), \tag{22b}$$

where $\zeta_r = \sum_i M_i(l_{ir1}m_{ir2} - l_{ir2}m_{ir1})$.

The solution to the zero-order Schrödinger equation is known[7] to be:

$$\Psi = \prod_s \exp(-q_s^2/2) H_{v_s}(q_s) \prod_r \exp(-\rho_r^2/2) R_{v_r l_r}(\rho_r) \exp(\pm i l_r \chi_r) \Psi_R^0, \tag{23}$$

where $H_{v_s}(q_s)$ are the Hermite polynomials and $R_{v_r l_r}(\rho_r) = \rho_r^{l_r} F(\rho_r)$, $F(\rho_r)$ being the associated Laguerre polynomial. In the latter case l_r may be regarded as a quantum number of internal angular momentum. It takes the values v_r, $v_r - 2$, $\cdots 0$, or 1. Ψ_R^0 in (23) is the characteristic function of the last part of (22a). The function Ψ_R^0 is most conveniently expressed as an expansion

$$\sum_{K=-J}^{K=+J} A_{JKM}^{(\tau)} \psi^0(J, K, M)$$

where $\psi^0(J, K, M)$ are the known solutions to the problem of the symmetric rotator which forms a complete orthogonal set of functions. In the above functions J, K and M are, respectively, the quantum numbers of total angular momentum, the quantum number of angular momentum about a body fixed axis and the so-called magnetic quantum number. τ is an index number running from $-J$ to $+J$ and $A_{J,K,M}^{(\tau)}$ are constants.

To find the eigenvalues of H_0 and the values of $A_{J,K,M}^{(\tau)}$ it is easiest to follow Wang[8] and set up the matrix H_0 in terms of the basic wave functions $\psi(v)\psi^0(J, K, M)$ where, of course, $\psi^0(J, K, M)$ will not in general be a solution to the rotation problem. The resulting matrix will in general not be a diagonal matrix, but will have the elements:

$$(v, l, J, M, K|H_0|v, l, J, M, K) = h \sum_s \lambda_s^{\frac{1}{2}}(v_s + g_s/2) + J(J+1)(\hbar^2/4)[(1/I_{xx}^{(e)}) + (1/I_{yy}^{(e)})] + (K^2\hbar^2/2)\{(1/I_{zz}^{(e)}) - \tfrac{1}{2}[(1/I_{xx}^{(e)}) + (1/I_{yy}^{(e)})]\}, \tag{24}$$

$$(v, l, J, M, K|H_0|v, l, J, M, K \pm 2) = (\hbar^2/8)[(1/I_{xx}^{(e)}) - (1/I_{yy}^{(e)})][f - K(K \pm 1)]^{\frac{1}{2}}[f - (K \pm 1)(K \pm 2)]^{\frac{1}{2}},$$

where v and l are taken to embrace all the vibration quantum numbers and g_s is the order of the degeneracy of the vibration frequency ω_s. An inspection of the elements (24) will reveal that for each value of the quantum number v and l the matrix will consist of steps, one step for each value of J. Since the elements (24) are independent of the quantum number M which may take all values from $-J$ to $+J$ it is evident that each step will be repeated $2J+1$ times. The energies $E_0(v, l, J, \tau)$ for the molecule may now be had simply by diagonalizing H_0, or which is the equivalent, by setting equal to zero the secular determinant of this matrix $|(K|H_0|K') - E\delta_{KK'}|$, $\delta_{KK'}$ being the Kronecker symbol, and determining the roots. The function Ψ_R^0 is now uniquely determined also, for the coefficients $A_{J,K,M}^{(\tau)}$ are simply the first minors of the above determinant.

Using the same basic wave functions we may arrive at the first-order corrections to the energy matrix. The only non-vanishing elements are the following:

$$(v, l, J, M, K|H_1'|v, l, J, M, K) = \sum_r \mp \zeta_r l_r K \hbar^2 / I_{zz}^{(e)}, \tag{25}$$

which lie along the principal diagonal. Since H_1' has elements only along the principal diagonal the second-order corrections can be determined by a first-order perturbation calculation using the wave functions (23). The function $\psi(J, K, M)$, as we have seen is really not a solution to the rotation problem; hence H_2' will contribute also to the elements of H which do not lie along the principal

[7] D. M. Dennison, Phys. Rev. **41**, 304 (1932).
[8] S. C. Wang, Phys. Rev. **34**, 243 (1929).

diagonal. H_2' is, however, diagonal in all the quantum numbers except the quantum number K and the only non-vanishing elements are the elements $(K|K)$, $(K|K\pm2)$ and $(K|K\pm4)$. When the zero-, first- and second-order contributions are combined one obtains for the elements of the entire energy matrix accurate to second order of approximation the following:

$$
\begin{aligned}
&(K|H|K)=\{R_0\mp R_1K+R_2K^2+R_3K^4\},\\
&(K|H|K\pm2)=\{[f-K(K\pm1)][f-(K\pm1)(K\pm2)]\}^{\frac{1}{2}}\{R_4+R_5[K^2+(K\pm2)^2]\},\\
&(K|H|K\pm4)=\{[f-K(K\pm1)][f-(K\pm1)(K\pm2)][f-(K\pm2)(K\pm3)][f-(K\pm3)(K\pm4)]\}^{\frac{1}{2}}R_6,
\end{aligned}
\tag{26}
$$

where

$$
\begin{aligned}
&R_0=(E_v/hc)+\tfrac{1}{2}(X_v+Y_v)J(J+1)-D_JJ^2(J+1)^2,\quad R_1=2Z_e\textstyle\sum_r\zeta_rl_r,\\
&R_2=Z_v-\tfrac{1}{2}(X_v+Y_v)-D_{JK}J(J+1),\quad R_3=-D_K,\quad R_4=(1/4)(X_v-Y_v)-\delta_JJ(J+1),\\
&R_5=(h/512\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)\{(a_{s\sigma}/(I_{zz}^{(e)})^2)^2-(b_{s\sigma}/(I_{yy}^{(e)})^2)^2-2(a_{s\sigma}c_{s\sigma}-2f_{s\sigma}^2)/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2\\
&\qquad\qquad+2(b_{s\sigma}c_{s\sigma}-2e_{s\sigma}^2)/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2\},\\
&R_6=(-h^3/1024\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)\{(a_{s\sigma}/(I_{zz}^{(e)})^2+b_{s\sigma}/(I_{yy}^{(e)})^2)^2-4d_{s\sigma}^2/(I_{zz}^{(e)})^2(I_{yy}^{(e)})^2\}.
\end{aligned}
\tag{27}
$$

The quantities occurring in (27) are defined in the following manner:

$$
X_v=X_e-\mathrm{x}_0-\sum_{s\sigma}\mathrm{x}_{s\sigma}(v_s+g_s/2),\quad Y_v=Y_e-\mathrm{y}_0-\sum_{s\sigma}\mathrm{y}_{s\sigma}(v_s+g_s/2),\quad Z_v=Z_e-\mathrm{z}_0-\sum_{s\sigma}\mathrm{z}_{s\sigma}(v_s+g_s/2),
$$

where

$$
X_e=h/8\pi^2cI_{xx}^{(e)},\quad Y_e=h/8\pi^2cI_{yy}^{(e)},\quad Z_e=h/8\pi^2cI_{zz}^{(e)},
$$

and where

$$
\begin{aligned}
\mathrm{x}_0&=(-h^3/256\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[(a_{s\sigma}/(I_{zz}^{(e)})^2-b_{s\sigma}/(I_{yy}^{(e)})^2)^2+4d_{s\sigma}^2/(I_{zz}^{(e)})^2(I_{yy}^{(e)})^2\\
&\qquad-12f_{s\sigma}^2/(I_{zz}^{(e)})^2(I_{yy}^{(e)})^2+8e_{s\sigma}^2/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2],\\
\mathrm{y}_0&=(-h^3/256\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[(a_{s\sigma}/(I_{zz}^{(e)})^2-b_{s\sigma}/(I_{yy}^{(e)})^2)^2+4d_{s\sigma}^2/(I_{zz}^{(e)})^2(I_{yy}^{(e)})^2\\
&\qquad+8f_{s\sigma}^2/(I_{zz}^{(e)})^2(I_{zz}^{(e)})^2-12e_{s\sigma}^2/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2],\\
\mathrm{z}_0&=(h^3/256\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[(3/2)(a_{s\sigma}/(I_{zz}^{(e)})^2-b_{s\sigma}/(I_{yy}^{(e)})^2)^2+6d_{s\sigma}^2/(I_{zz}^{(e)})^2(I_{yy}^{(e)})^2\\
&\qquad-16(f_{s\sigma}^2/(I_{zz}^{(e)})^2(I_{zz}^{(e)})^2+e_{s\sigma}^2/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2)],
\end{aligned}
\tag{28}
$$

$$
\begin{aligned}
\mathrm{x}_{s\sigma}&=X_e\sum_{s'\sigma'}{}'(h/4\pi^2cg_sI_{zz}^{(e)}\omega_s)\{[A_{s\sigma s\sigma}-(a_{s\sigma}^2/I_{zz}^{(e)})-(d_{s\sigma}^2/I_{yy}^{(e)})-(f_{s\sigma}^2/I_{zz}^{(e)})]-3a_{s\sigma}k_{s\sigma s}/4\pi^2c^2\omega_s^2\\
&\quad-a_{s'\sigma'}k_{s's\sigma}/4\pi^2c^2\omega_{s'}^2-\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})\sum_{i'}M_{i'}(m_{i's\sigma}n_{i's'\sigma'}-m_{i's'\sigma'}n_{i's\sigma})\\
&\qquad\times(3\omega_s^2+\omega_{s'}^2)/(\omega_s^2-\omega_{s'}^2)\},\\
\mathrm{y}_{s\sigma}&=Y_e\sum_{s'\sigma'}{}'(h/4\pi^2cg_sI_{yy}^{(e)}\omega_s)\{[B_{s\sigma s\sigma}-(d_{s\sigma}^2/I_{zz}^{(e)})-(b_{s\sigma}^2/I_{yy}^{(e)})-(e_{s\sigma}^2/I_{zz}^{(e)})]-3b_{s\sigma}k_{s\sigma s}/4\pi^2c^2\omega_s^2\\
&\quad-b_{s'\sigma'}k_{s's\sigma}/4\pi^2c^2\omega_{s'}^2-\sum_i M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma'}l_{is\sigma})\sum_{i'}M_{i'}(n_{i's\sigma}l_{i's'\sigma'}-n_{i's'\sigma'}l_{i's\sigma})\\
&\qquad\times(3\omega_s^2+\omega_{s'}^2)/(\omega_s^2-\omega_{s'}^2)\},
\end{aligned}
$$

$$z_{ss}=Z_e\sum_{s'\sigma'}{}'(h/4\pi^2cg_sI_{zz}^{(e)}\omega_s)\{[C_{ssss}-(f_{ss}^2/I_{xx}^{(e)})-(e_{ss}^2/I_{yy}^{(e)})-(c_{ss}^2/I_{zz}^{(e)})]-3c_{ss}k_{sss}/4\pi^2c^2\omega_s^2$$
$$-c_{s's'}k_{s'ss}/4\pi^2c^2\omega_{s'}^2-\sum_i M_i(l_{iss}m_{is's'}-l_{is's'}m_{iss})\sum_{i'}M_{i'}(l_{i'ss}m_{i's's'}-l_{i's's'}m_{iss})$$
$$\times(3\omega_s^2+\omega_{s'}^2)/(\omega_s^2-\omega_{s'}^2)\},$$

$$D_J=(h^3/512\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[3a_{ss}^2/(I_{xx}^{(e)})^4+3b_{ss}^2/(I_{yy}^{(e)})^4+2(a_{ss}b_{ss}+2d_{ss}^2)/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2],$$

$$D_{JK}=-2D_J+(h^3/64\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[(a_{ss}c_{ss}+2f_{ss}^2)/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2+(b_{ss}c_{ss}+2e_{ss}^2)/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2],$$

$$D_K=D_J+(h^3/64\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[(c_{ss}^2/(I_{zz}^{(e)})^4-(a_{ss}c_{ss}+2f_{ss}^2)/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2$$
$$-(b_{ss}c_{ss}+2e_{ss}^2)/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2],$$

$$\delta_J=(h^3/256\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[(a_{ss}^2/(I_{xx}^{(e)})^4)-(b_{ss}^2/(I_{yy}^{(e)})^4)].$$

The quantity E_v in (27) is the vibration energy of the molecule and may be written:

$$(E_v/hc)=(E_0/hc)+\sum_s\omega_s(v_s+g_s/2)+\sum_s\sum_{s'}x_{ss'}(v_s+g_s/2)(v_{s'}+g_{s'}/2)+\sum_r\sum_{r'}x_{l_rl_r'}l_rl_{r'} \tag{29}$$

in which

$$x_{ss}=(h/32\pi^4\omega_s^2c^3)\{3k_{ssss}-(15k_{sss}^2/8\pi^2c^2\omega_s^2)-\sum_{s'}(k_{sss'}^2/4\pi^2c^2\omega_{s'}^2)+\sum_{s'}(k_{sss'}^2/8\pi^2c^2(4\omega_s^2-\omega_{s'}^2))\},$$

$$x_{ss'}=(h/32\pi^4\omega_s\omega_{s'}c^3)\{k_{sss's'}-(6k_{sss}k_{ss's'}/4\pi^2c^2\omega_s^2)-\sum_{s''}{}'(k_{sss''}k_{s''s's'}/4\pi^2c^2\omega_{s''}^2)$$
$$-(k_{sss'}^2/\pi^2c^2(4\omega_s^2-\omega_{s'}^2)+\sum_{s''}{}'k_{ss's''}^2(\omega_{s''}^2-\omega_{s'}^2-\omega_s^2)/4\pi^2c^2(\omega_s+\omega_{s'}+\omega_{s''})(\omega_s+\omega_{s'}-\omega_{s''})$$
$$\times(\omega_s-\omega_{s'}+\omega_{s''})(\omega_s-\omega_{s'}-\omega_{s''})+4\pi^2c^2\sum_{s\sigma s'}(\omega_{s'}^2/g_sg_{s'}I_{xx}^{(e)})\sum_i M_i(m_{iss}n_{is's'}-m_{is's'}n_{iss})$$
$$\times\sum_{i''}M_{i''}(m_{i''ss}n_{i''s's'}-m_{i''s's'}n_{i''ss})+4\pi^2c^2\sum_{s\sigma s'}(\omega_{s'}^2/g_sg_{s'}I_{yy}^{(e)})\sum_i M_i(n_{iss}l_{is's'}-n_{is's'}l_{iss}) \tag{30}$$
$$\times\sum_{i''}M_{i''}(n_{i''ss}l_{i''s's'}-n_{i''s's'}l_{i''ss})+4\pi^2c^2\sum_{s\sigma s'}(\omega_{s'}^2/g_sg_{s'}I_{zz}^{(e)})\sum_i M_i(l_{iss}m_{is's'}-l_{is's'}m_{iss})$$
$$\times\sum_{i''}M_{i''}(l_{i''ss}m_{i''s's'}-l_{i''s's'}m_{i''ss})\},$$

$$x_{l_rl_r}=(-h/32\pi^4\omega_r^2c^3)\{k_{rrrr}+\sum_{s'}(k_{rrs'}^2/8\pi^2c^2(4\pi\omega_r^2-\omega_{s'}^2))-(4\pi^2c^2\omega_r^2/I_{zz}^{(e)})$$
$$\times\sum_i M_i(l_{ir1}m_{ir2}-l_{ir2}m_{ir1})\sum_{i''}M_{i''}(l_{i''r1}m_{i''r2}-l_{i''r2}m_{i''r1})\},$$

$$x_{l_rl_{r'}}=(h/8\pi^2I_{zz}^{(e)})\sum_i M_i(l_{ir1}m_{ir2}-l_{ir2}m_{ir1})\sum_{i''}M_{i''}(l_{i''r'1}m_{i''r'2}-l_{i''r'2}m_{i''r'1}).$$

(E_0/hc) is a constant term depending in a very complicated manner on the potential energy constants and since in practice one is only interested in differences between energies and not in their absolute values this term is not set down.

As in the case of H_0, for a given value of the quantum numbers v and l the above matrix will consist of steps, one step for each value of J. As before, the energy is independent of the quantum

number M so that each step will be repeated $2J+1$ times. For a given value of J the actual energy values may now be obtained as in the zero-order problem, i.e., by diagonalizing the matrix H. This again is accomplished by setting the secular determinant $|(K|H|K')-E\delta_{KK'}|$ equal to zero and solving for the roots. This determinant will resemble the Wang-Klein determinant for the asymmetric rotator, but will be considerably more complicated in general. The determinant can at once be factored into sub-steps corresponding to given values of the quantity $\sum_r l_r$ and each step will be repeated twice, once for the positive value and once for the negative value of $\sum_r l_r$. Each of these sub-steps can further be factored simply by arranging the rows and columns so that the even values of K stand together and the odd values of K stand together. The elements of the Wang-Klein determinant are independent of the algebraic sign of K so that a further factorization is possible. It may be seen that because of the term $\sum_r(\zeta_r l_r K/I_{zz}^{(e)})$ in the diagonal elements this is no longer true in the general case and no further factorization is at once possible.

Darling and Dennison have pointed out that for a molecule like the H_2O moleculate a relation $\Delta=I_{xx}^{(e)}+I_{yy}^{(e)}-I_{zz}^{(e)}$ $(I_{xx}^{(e)}<I_{yy}^{(e)}<I_{zz}^{(e)})$ exists such that Δ is independent to this approximation of the anharmonic constants. That such a relation exists in general for all planar molecules may be verified from the relations (28) by setting $\overset{0}{z}_i=0$ in which case $a_{s\sigma}+b_{s\sigma}-c_{s\sigma}=0$. Such relations will not exist in general for non-planar molecules.

IV. The Vibration-Rotation Energies in Special Types of Molecules

A. Asymmetric molecules

In the case of asymmetric molecules the atoms assume such geometric configurations that the three moments of inertia $I_{xx}^{(e)}$, $I_{yy}^{(e)}$ and $I_{zz}^{(e)}$ are all different from each other. In such cases, however, it is true almost without exception that there are no degenerate frequencies. There will therefore be only a single coordinate q_{s1} associated with a frequency ω_s, i.e., the index σ takes only the value $\sigma=1$. When this is so the terms which would occur in H_1' will all vanish and hence the elements in the matrix H will become entirely independent of the sign of K. Except in cases where two vibration frequencies become accidentally degenerate the sub-steps of the secular determinant of the matrix H can be further factored as pointed out by Shaffer and Nielsen with reference to the triatomic non-linear molecule. When results of this kind are to be applied to experimental data it is frequently desirable to expand the secular determinant of the energies into a set of algebraic equations. This has been done by Nielsen[9] for the triatomic non-linear molecule for the values of J up to and including $J=6$. It is found that these same equations are valid in the case of the general asymmetric molecule except that the more general definitions of the R_i given in (26) must be used and that ϵ is here equal to $(2E/h^2-R_0)$.

B. Axially symmetric molecules

In molecules belonging to this important classification the geometric arrangement of the atoms is such that the two moments of inertia $I_{xx}^{(e)}$ and $I_{yy}^{(e)}$ are equal to each other while $I_{zz}^{(e)}$ will in general be different. In the case of such molecules the $(K|K\pm2)$ elements will always vanish except for second-order terms.[10] The $(K|K\pm4)$ elements are also of the same order of magnitude. It is found that when the secular determinant for the energies is expanded that the elements off of the principal diagonal can contribute only in an approximation higher than the second. For our purpose they may therefore legitimately be neglected. This is equivalent to stating that to second order of approxima-

[9] H. H. Nielsen, Phys. Rev. **59**, 565 (1941).

[10] Shaffer and Silver have found that in the case of the planar XY_3, the pyramidal XY_3 type and the axially symmetric XY_3Z type molecules these elements vanish identically even to second order of approximation. Reference to the definitions of x_0, y_0, $x_{s\sigma}$ and $y_{s\sigma}$ [Eq. (28)] makes it seem plausible that to second order at least this is always true.

tion a molecule which is a symmetric rotator when the atoms are in their equilibrium positions will effectively remain a symmetric rotator also in higher vibration-rotation states. The vibration-rotation energies of such a molecule are then just the diagonal elements of (26) of the energy matrix. For such molecules it is convenient to state them in the following manner:

$$(E/hc)=(E_v/hc)+(E_{\text{rot}}/hc)\mp(h/4\pi^2 cI_{zz}^{(e)})\textstyle\sum_r \zeta_r l_r K. \tag{31}$$

where (E_v/hc) is the same as that given by (29) and (30) and where

$$(E_{\text{rot}}/hc)=J(J+1)B_v-K^2(B_v-C_v)-J^2(J+1)^2D_J-J(J+1)K^2D_{JK}-K^4D_K \tag{32}$$

in which

$$\begin{aligned}
&B_v=B_e-\alpha_0-\textstyle\sum_s(v_s+g_s/2)\alpha_s,\\
&C_v=C_e-\gamma_0-\textstyle\sum_s(v_s+g_s/2)\gamma_s,\\
&B_e=(h/8\pi^2 I_{xx}^{(e)}c),\quad (I_{xx}^{(e)}=I_{yy}^{(e)}),\\
&C_e=(h/8\pi^2 I_{zz}^{(e)}c),\\
&\alpha_0=\tfrac{1}{2}(\mathrm{x}_0+\mathrm{y}_0),\qquad \gamma_0=\mathrm{z}_0,\\
&\alpha_s=\tfrac{1}{2}\textstyle\sum_\sigma(\mathrm{x}_{s\sigma}+\mathrm{y}_{s\sigma}),\ \gamma_s=\sum_\sigma \mathrm{z}_{s\sigma},
\end{aligned} \tag{33}$$

and where D_J, D_{JK} and D_K are defined as in (28).

C. The linear polyatomic molecule.

Linear polyatomic molecules constitute a group which may be regarded as special cases of the axially symmetric molecules. In molecules of this type $p_z-P_z=0$, i.e., $p_z=P_z=(\mp ih)\sum_r l_r$ and from this restriction it is easily shown that all terms involving $I_{zz}^{(e)}$, $e_{s\sigma}$ and $f_{s\sigma}$ will vanish from the Hamiltonian function, H, and hence also from the elements of the energy matrix. The moments of inertia $I_{xx}^{(e)}$ and $I_{yy}^{(e)}$ will be alike so that there will also here be no elements off of the principal diagonal. The vibration-rotation energies of linear polyatomic molecules may therefore conveniently be written:

$$(E/hc)=(E_{\text{vib}}/hc)+(E_{\text{rot}}/hc), \tag{34}$$

where

$$(E_{\text{vib}}/hc)=(E_0/hc)+\textstyle\sum_s\omega_s(v_s+g_s/2)+\sum_s\sum_{s'}x_{ss'}(v_s+g_s/2)(v_{s'}+g_{s'}/2)+\sum_r x_{l_rl_r}l_r^2, \tag{35}$$

in which

$$x_{ss}=(h/32\pi^4 c^3\omega_s^2)\{3k_{ssss}-15k_{sss}^2/8\pi^2c^2\omega_s^2-\textstyle\sum_{s'}k_{sss'}^2/4\pi^2c^2\omega_{s'}^2+\sum_{s'}k_{sss'}^2/8\pi^2c^2(4\omega_s^2-\omega_{s'}^2)\},$$

$$\begin{aligned}
x_{ss'}=(h/32\pi^4c^3\omega_s\omega_{s'})\{&k_{sss's'}-6k_{sss}k_{ss's'}/4\pi^2c^2\omega_s^2-\textstyle\sum_{s''}{}'k_{sss''}k_{s's's''}/4\pi^2c^2\omega_{s''}^2-k_{sss'}^2/\pi^2c^2(4\omega_s^2-\omega_{s'}^2)\\
&+\textstyle\sum_{s''}{}'k_{ss's''}^2(\omega_{s''}^2-\omega_{s'}^2-\omega_s^2)/4\pi^2c^2(\omega_s+\omega_{s'}+\omega_{s''})(\omega_s+\omega_{s'}-\omega_{s''})(\omega_s-\omega_{s'}+\omega_{s''})(\omega_s-\omega_{s'}-\omega_{s''})\\
&+4\pi^2c^2\textstyle\sum_{\sigma\sigma'}(\omega_{s'}^2/g_sg_{s'}I_{zz}^{(e)})[\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})\sum_{i''}M_{i''}(m_{i''s\sigma}n_{i''s'\sigma'}-m_{i''s'\sigma'}n_{i''s\sigma})\\
&+\textstyle\sum_i M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma'}l_{is\sigma})\sum_{i''}M_{i''}(n_{i''s\sigma}l_{i''s'\sigma'}-n_{i''s'\sigma'}l_{i''s\sigma})]\},
\end{aligned}$$

$$x_{l_rl_r}=(-h/32\pi^4c^3\omega_r^2)\{k_{rrrr}+\textstyle\sum_{s'}k_{rrs'}/8\pi^2c^2(4\omega_r^2-\omega_{s'}^2)\},$$

and where

$$(E_{\text{rot}}/hc)=[J(J+1)-l^2]B_v-[J(J+1)-l^2]^2D, \tag{36}$$

in which

$$B_v=B_e-\sum_s (v_s+g_s/2)\alpha_s, \tag{37}$$

$$B_e=h/8\pi^2 cI_{xx}^{(e)},$$

$$\alpha_s=B_e(h/4\pi^2 c\omega_s g_s I_{xx}^{(e)})\sum_\sigma\{[A_{ss\sigma}-((a_{ss}^2+d_{ss}^2)/I_{xx}^{(e)})]-3a_{ss}k_{sss}/4\pi^2 c^2\omega_s^2$$
$$+g_s\sum_{s'}\sum_{\sigma'}(a_{s'\sigma'}k_{s'ss}/4\pi^2 c^2\omega_{s'}^2)-\sum_{s'}\sum_{\sigma'}[\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})$$
$$\times\sum_{i'}M_{i'}(m_{i's\sigma}n_{i's'\sigma'}-m_{i's'\sigma'}n_{i's\sigma})](3\omega_s^2+\omega_{s'}^2)/(\omega_s^2-\omega_{s'}^2)\},$$

$$D=(h^3/128\pi^6 c^3)\sum_{s,\sigma}(1/8\omega_s^2)(2a_{ss}^2+d_{ss}^2)/(I_{xx}^{(e)})^4,$$

$$l=\sum_r l_r.$$

V. Conclusion

In the preceding sections relations have been derived for the vibration-rotation energies of a general polyatomic molecule to second order of approximation. These relations have been used to verify the results arrived at independently by various authors for certain molecular models and in each case have been found to corroborate their results. Enough cases have been tested by the author to verify the contributions from each kind of term in the Hamiltonian, H, and this is deemed a convincing check on the accuracy of the calculations here reported upon. In each of the cases tested by the author it was found that the vibration-rotation energies could be deduced in a small fraction of the time required to obtain them by the Howard and Wilson method starting at the beginning.

It will be seen by inspection of the relations (26–30) that two and only two types of resonances occur in the energies to this approximation. These are of the Fermi-Dennison[11] type and of the Coriolis resonance type. The first is a resonance between a fundamental frequency ω_r and a combination frequency $\omega_s+\omega_t$, i.e., the resonance denominator will contain $(\omega_r-\omega_s-\omega_t)$. Such terms will shift the centers of the vibrations bands, but will leave the spacings between rotation lines essentially unchanged. The second type is a resonance between two fundamental frequencies, e.g., $(\omega_r-\omega_s)$. This kind of term will alter the effective moments of inertia and may therefore give rise to anomolous spacings between the rotational lines. Essentially, however, it will not alter the positions of the band centers. Whenever the resonance denominators $\omega_r-\omega_s-\omega_t$ and $\omega_r-\omega_s$, respectively, become too small the usual methods of perturbation theory fail and other methods of procedure must be resorted to. While to this order of approximation these are the only resonances which can occur, resonances may, of course, also occur in higher approximations and may probably also make themselves felt in the spectrum.

It is pertinent here to inquire into the practicability of carrying such calculations to still higher orders of approximation. It is doubtful whether such calculations would be particularly useful since in a higher approximation it appears that the secular determinant for the energies would contain elements of the kind $(K|K)$, $(K|K\pm1)$, $(K|K\pm2)$, etc. This would mean that the secular determinant would not factor into sub-steps and that the work involved in determining the energies would become prohibitive.

Moreover, in another approximation interactions between the electronic motions and the motion of vibration and rotation might be expected to set in and these certainly would be difficult to take satisfactorily into account. Also the approximation used throughout these and other similar calcu-

[11] E. Fermi, Zeits. f. Physik **71**, 250 (1931).

lations that the oscillators are approximated by simple harmonic oscillators where the variables $q_{s\sigma}$ extend from $+\infty$ to $-\infty$ rather than from q_0 to $+\infty$ would begin to become invalid in higher approximations.[12] Finally the approximation made earlier that coefficients multiplying functions of $q_{s\sigma}$ in H_1, which themselves are functions of P_α, may be treated as constant coefficients becomes inadequate. This convenient approximation is satisfactory so long as the energies are not estimated beyond the second order, but in still higher orders of approximation the non-commutative character of H_{0R} and P_α may become significant. It appears, therefore, that in general the work which would be required to extend calculations of this kind to approximations higher than the second would become prohibitive.

Appendix

It has seemed worth while to insert an example to illustrate how the results derived in the foregoing sections may be used to obtain the vibration-rotation energies in a particular case. The example chosen pertains to the planar XY_3 type molecule which already has been studied by Silver and Shaffer[1] (S. and S.). In their work the plane of the molecule is made to coincide with the xy plane of the body fixed axes so that the z axis becomes the axis of symmetry. The configuration is so oriented that the equilibrium positions of the Y particles and the X particle will be, respectively $(-a, 0, 0)$; $(a/2, -3^{\frac{1}{2}}a/2, 0)$; $(a/2, 3^{\frac{1}{2}}a/2, 0)$; $(0, 0, 0)$.

From the foregoing work it is possible to write the displacements of the particles X and Y along the x, y and z coordinates in terms of the normal coordinates $Q_{s\sigma}$ as follows:

$$\delta x_i = \sum_i l_{is\sigma} Q_{s\sigma}, \quad \delta y_i = \sum_i m_{is\sigma} Q_{s\sigma}, \quad \delta z_i = \sum_i n_{is\sigma} Q_{s\sigma},$$

where the $l_{is\sigma}$, $m_{is\sigma}$ and $n_{is\sigma}$ are the following:

$$l_{11}[13] = (3M)^{-\frac{1}{2}}, \qquad l_{121} = (3M)^{-\frac{1}{2}}[(m/(3M+m))^{\frac{1}{2}}\gamma - \delta], \quad l_{122} = 0,$$

$$l_{141} = (3M)^{-\frac{1}{2}}[(m/(3M+m))^{\frac{1}{2}}\delta + \gamma], \quad l_{142} = 0,$$

$$l_{21} = -\tfrac{1}{2}(3M)^{-\frac{1}{2}}, \quad l_{221} = (3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\gamma + \frac{\delta}{2}\right], \quad l_{222} = \frac{\delta}{2}(M)^{-\frac{1}{2}},$$

$$l_{241} = (3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\delta - \frac{\gamma}{2}\right], \quad l_{242} = -\frac{\gamma}{2}(M)^{-\frac{1}{2}},$$

$$l_{31} = -\tfrac{1}{2}(3M)^{-\frac{1}{2}}, \quad l_{321} = (3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\gamma + \frac{\delta}{2}\right], \quad l_{322} = -\frac{\delta}{2}(M)^{-\frac{1}{2}},$$

$$l_{341} = (3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\delta - \frac{\gamma}{2}\right], \quad l_{342} = \frac{\gamma}{2}(M)^{-\frac{1}{2}},$$

$$l_{41} = 0, \qquad l_{421} = -m^{-\frac{1}{2}}(3M/(3M+m))^{\frac{1}{2}}\gamma, \qquad l_{422} = 0,$$

$$l_{441} = -m^{-\frac{1}{2}}(3M/(3M+m))^{\frac{1}{2}}\delta, \qquad l_{442} = 0,$$

$$l_{13} = l_{23} = l_{33} = l_{43} = 0, \tag{A1}$$

$$m_{11} = 0, \qquad m_{121} = 0, \qquad m_{122} = (3M)^{-\frac{1}{2}}[(m/(3M+m))^{\frac{1}{2}}\gamma + \delta], \quad m_{141} = 0,$$

$$m_{142} = (3M)^{-\frac{1}{2}}[(m/(3M+m))^{\frac{1}{2}}\delta - \gamma],$$

$$m_{21} = \tfrac{1}{2}(M)^{-\frac{1}{2}}, \quad m_{221} = \frac{\delta}{2}(M)^{-\frac{1}{2}}, \quad m_{222} = (3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\gamma - \frac{\delta}{2}\right], \quad m_{241} = -\frac{\gamma}{2}(M)^{-\frac{1}{2}},$$

$$m_{242} = (3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\delta + \frac{\gamma}{2}\right],$$

[12] I am indebted to Professor L. H. Thomas for this information.

[13] In the case of the frequencies ω_1 and ω_3 which are non-degenerate the index σ takes only the value $\sigma = 1$. It is convenient in such cases to omit the index since no ambiguity arises out of so doing.

$$m_{31}=-\tfrac{1}{2}(M)^{-\frac{1}{2}},\quad m_{321}=-\frac{\delta}{2}(M)^{-\frac{1}{2}},\quad m_{322}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\gamma-\frac{\delta}{2}\right],\quad m_{341}=\frac{\gamma}{2}(M)^{-\frac{1}{2}},$$

$$m_{342}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}+\frac{\gamma}{2}\right],$$

$$m_{41}=0,\qquad m_{421}=0,\qquad m_{422}=-m^{-\frac{1}{2}}(3M/(3M+m))\gamma,\qquad m_{441}=0,$$

$$m_{442}=-m^{-\frac{1}{2}}(3M/(3M+m))^{-\frac{1}{2}}\delta,$$

$$m_{13}=m_{23}=m_{33}=m_{43}=0,$$

$$n_{13}=n_{23}=n_{33}=(3M)^{-\frac{1}{2}}(m/(3M+m))^{\frac{1}{2}},\quad n_{43}=-m^{-\frac{1}{2}}(3M/(3M+m))^{\frac{1}{2}},\quad n_{s\sigma}=0\quad(s\neq 3),$$

M and m being the masses, respectively, of the Y and X particles and δ and γ being transformation constants.

The first step in evaluating the energies is to determine the values of $a_{s\sigma}$, $b_{s\sigma}$, etc. and $A_{s\sigma s'\sigma'}$, $B_{s\sigma s'\sigma'}$, etc. We shall evaluate only one of these, namely, a_{21} and A_{2222}. The first of these is:

$$a_{21}=2(M\overset{0}{y}_1 m_{121}+M\overset{0}{y}_2 m_{221}+M\overset{0}{y}_3 m_{321}+m\overset{0}{y}_4 m_{421}).$$

Since $m_{121}=m_{421}=0$ and $\overset{0}{y}_3=-\overset{0}{y}_2$ we obtain:

$$a_{21}=2(M)^{\frac{1}{2}}\overset{0}{y}_2\delta=-(I_{zz}^{(e)})^{\frac{1}{2}}\delta. \tag{A2}$$

In a similar manner we find that

$$a_1=b_1=-(I_{zz}^{(e)})^{\frac{1}{2}},\quad b_{21}=-a_{21},\quad a_{41}=-b_{41}=(I_{zz}^{(e)})^{\frac{1}{2}}\gamma,\quad a_{22}=b_{22}=a_3=b_3=a_{42}=b_{42}=0,\quad c_1=a_1+b_1,$$

$c_{s\sigma}=0(s\neq 1)$. The constant A_{2222} is defined by (15) and in our particular case it becomes:

$$A_{2222}=\{(1/3)[(3m/(3M+m))\gamma^2+3\delta^2/2]+(3M/(3M+m))\gamma^2\}$$

$$-\{(m/(3M+m))\gamma+(3M/(3M+m))\gamma\}^2=\delta^2/2. \tag{A3}$$

Likewise one finds that $A_{11}=B_{11}=\frac{1}{2}$, $A_{2121}=A_{2222}=B_{2121}=B_{2222}=\delta^2/2$, $A_{3333}=B_{3333}=0$, $A_{4141}=A_{4242}=B_{4141}=B_{4242}=\gamma^2/2$, $C_{11}=1$, $C_{s\sigma s\sigma}=0$ $(s\neq 1)$.

We shall next compute the values of ζ_2 and ζ_4 which occur in the first order energies. By definition $\zeta_2=\sum_{i=1}^{4} M_i(l_{i21}m_{i22}-l_{i22}m_{i21})$. With the values of $l_{is\sigma}$ and $m_{is\sigma}$ given in (A1) one obtains at once $\zeta_2=(\gamma^2-\delta^2)$. In the same way one verifies that $\zeta_4=-\zeta_2$.

The vibration term values are given by the relations (29) where the constants $x_{s\sigma'}$ and $x_{l,l'}$ depend upon the coefficients occurring in the anharmonic part of the potential energy. We shall evaluate only two of these, namely, $x_{3,4}$ and $x_{4,3}$. Inspection of the anharmonic part of the potential energy function adopted by S. and S. shows that the only k's which can occur in (30) are k_{4433}, k_{441} and k_{133}. Evidently

$$x_{3,4}=(h/32\pi^4\omega_3\omega_4 c^3)\{k_{3344}-k_{441}k_{133}/4\pi^2c^2\omega_1^2+4\pi^2c^2\omega_3^2([M(m_{241}n_{23}+m_{341}n_{33})]^2$$

$$+[M(m_{142}n_{13}+m_{242}n_{23}+m_{342}n_{23})+mm_{442}n_{43}]^2)\},$$

of which the last two terms reduce to $4\pi^2c^2\omega_3^2\delta^2$. The term x_{43} is entirely like x_{34} except that the last term is equal to $4\pi^2c^2\omega_4^2\delta^2$. The x_{34} and x_{43} are added together and if it is taken into account that $(h^2/\lambda_3^{\frac{1}{2}}\lambda_4^{\frac{1}{2}})k_{3344}=hc\gamma_{3344}$ and $(h^3/\lambda_1^{\frac{1}{2}}\lambda_3)^{\frac{1}{2}}k_{133}=hc\beta_{133}$ in the notation of S. and S. we have at once that $(x_{34}+x_{43})=(\delta^2h/8\pi^2I_{zz}^{(e)})(\omega_3/\omega_4+\omega_4/\omega_3)-\beta_{133}\beta_{144}/\omega_1+\gamma_{3344}$. In a similar fashion all the other G_{ik} obtained by S. and S. may be derived.

We shall then proceed to consider the rotational constants. This consists in evaluating the B_v and C_v as defined by S. and S. We shall here evaluate only B_v which is $B_e-\alpha_0-\sum_s (v_s+g_s/2)\alpha_s$, B_e being $(h/8\pi^2 I_{xx}^{(e)}c)$ since $I_{xx}^{(e)}=I_{yy}^{(e)}$. The constant α_0 will in our notation be $x_0=y_0$. From the relations (28) we have that:

$$x_0=(-h^3/256\pi^6 c^3)\sum_{s\sigma}(1/8\omega_s^2)\{[(a_{s\sigma}-b_{s\sigma})^2+4d_{s\sigma}^2]/(I_{xx}^{(e)})^4\}, \tag{A4}$$

which upon insertion of the values $a_{s\sigma}$, $b_{s\sigma}$ and $d_{s\sigma}$ leads immediately to the result:

$$x_0=y_0=\alpha_0=-4B_e^3(\delta^2/\omega_2^2+\gamma^2/\omega_4^2). \tag{A5}$$

We proceed to evaluate the α_i. In this appendix we shall evaluate only α_2 which will serve to demonstrate how the others may be obtained. We have:

$$x_{21}=X_e(h/8\pi^2 c\omega_2 I_{xx}^{(e)})[(\delta^2/2-2I_{xx}^{(e)}\delta^2/I_{xx}^{(e)})+(2)^{\frac{1}{2}}(I_{xx}^{(e)})^{\frac{1}{2}}k_{122}/4\pi^2 c^2\omega_1^2]$$

and

$$x_{22}=X_e(h/8\pi^2 c\omega_2 I_{xx}^{(e)})[(\delta^2/2-2I_{xx}^{(e)}\delta^2/I_{xx}^{(e)})+(2)^{\frac{1}{2}}(I_{xx}^{(e)})^{\frac{1}{2}}k_{122}/4\pi^2 c^2\omega_1^2$$
$$-(Mm_{122}n_{13}+Mm_{222}n_{23}+Mm_{322}n_{33}+mm_{422}n_{43})^2(3\omega_2^2+\omega_1^2)/(\omega_2^2-\omega_1^2)].$$

After inserting the values for $m_{is\sigma}$ and simplifying one obtains:

$$\alpha_2=(x_{21}+x_{22})=X_e(h/4\pi^2 c\omega_2 I_{xx}^{(e)})[(-3\delta^2/2)+(2I_{xx}^{(e)})^{\frac{1}{2}}k_{122}/4\pi^2 c^2\omega_1^2-\gamma^2(3\omega_2^2+\omega_1^2)/2(\omega_2^2-\omega_1^2)], \tag{A6}$$

which is equivalent to the expression of S. and S. for α_2.

Of the centrifugal stretching coefficients D we shall evaluate only D_J which is defined in Eqs. (28). It here becomes:

$$D_J=(h^3/512\pi^6 c^3)\{(1/8\omega_1^2)(16I_{xx}^{(e)}/(I_{xx}^{(e)})^4)+(1/8\omega_2^2)[(12I_{xx}^{(e)2}\delta^2-4I_{xx}^{(e)2}\delta^2+8I_{xx}^{(e)2}\delta^2)/(I_{xx}^{(e)})^4]+16I_{xx}^{(e)}\gamma^2/8\omega_4^2(I_{xx}^{(e)})^4\}$$

which becomes equal to

$$D_J=2B_e^3((1/\omega_1^2)+(\delta^2/\omega_2^2)+(\gamma^2/\omega_4^2)). \tag{A7}$$

It is easy to verify the relationship for D_K obtained by S. and S. and also their relation that $D_{JK}=(-2/3)(D_J+2D_K)$.

These constants being evaluated the vibration-rotation energies of the XY_3 planar molecule are determined and are given explicitly by the relations (31) and (32) in Section IV.

Increase of Residual Magnetism Caused by a Current Flowing Through an Iron Bar

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If a bar of high grade wrought iron or of permalloy is placed in a sufficiently strong magnetic field, and if this field is abruptly reduced to zero, a current set up in the iron causes an increase of the residual magnetism. This effect is not obtained when the field is gradually eliminated, nor is it obtained when the current flows in a wire along the axis of a bored out iron cylinder unless the cylinder is slotted longitudinally. Then the increase of magnetism is again observed. There seem to be two effects involved in this phenomenon. One of these results in decreasing the residual magnetism in accordance with Wiedeman's and Villari's observations, and is apparently associated with the circular flux set up in the bar by a current sent directly through it or in a separate wire along its axis. The other effect, if it could be completely isolated, would probably produce only increases in residual magnetism, and seems to depend on an unstable condition of the magnet.

INTRODUCTION

IT has long been known that a current of electricity sent through an iron bar or wire previously magnetized tends to reduce the residual magnetism much like the effect of a mechanical jar. In 1862 Wiedeman[1] described this decrease of residual magnetism, and also a less vigorous increase when the current through the iron was broken. In 1865 Villari[2] published the results of extensive investigations in the same field, and he too observed the decrease in residual magnetism caused by a longitudinal current, but does not seem to have observed the increase when the circuit was broken. A study of his tabulations shows that after the first "make" the galvanometer deflections (by which alterations of flux were observed) caused by subsequent and repeated "makes" and "breaks," rapidly approach the same constant value though in opposite senses. This is obviously a purely inductive effect and has nothing to do with changes in the residual magnetism. So, although Villari reports galvanometer deflections suggesting increased magnetization, they are always subsequent to the initial "make," while the significant deflection produced when the current was first established always indicates the expected decrease.

The phenomena just cited seem to be closely associated with the effect of mechanical stresses of various kinds upon the magnetic properties of iron, but in general a jar or twist or pull tends to diminish residual magnetism. However in his collected *Mathematical and Physical Papers*, Vol. II, page 351, Sir William Thomson (Lord Kelvin) reports an increase in residual magnetism when tension was suddenly applied to a previously magnetized wire of soft iron, whereas a steel wire showed the usual decrease. In a footnote he says he later concluded that this could be explained by the influence of terrestrial magnetism, but as we found the same increase when a bar of wrought iron received an end on tap, it would seem as if the effect really existed in certain kinds of iron.

During the summer of 1939 we undertook a further study of the effect of a current on residual magnetism, using at first a bar of permalloy given us by the Bell Telephone Laboratories, and later bars of very pure Norway iron, cast iron and nickel, the latter being the gift of the International Nickel Company. In the course of these observations we were very much surprised to find that when a cylindrical bar either of permalloy or of Norway iron had been magnetized beyond a certain minimum value by a solenoid whose current was then *suddenly* broken, an increase instead of a decrease of the residual magnetism was produced by a current sent through the iron in either direction. Two effects seem to be present. One of them which we shall call "effect *A*" operates with striking rapidity, and tends to increase the residual magnetism. The other "effect *B*" results in decreasing the residual magnetism and is definitely slower in its action.

[1] G. Wiedeman, Poggendorff's Annalen **117**, 215 (1862).
[2] E. Villari, Poggendorff's Annalen **126**, No. 9, (1865).

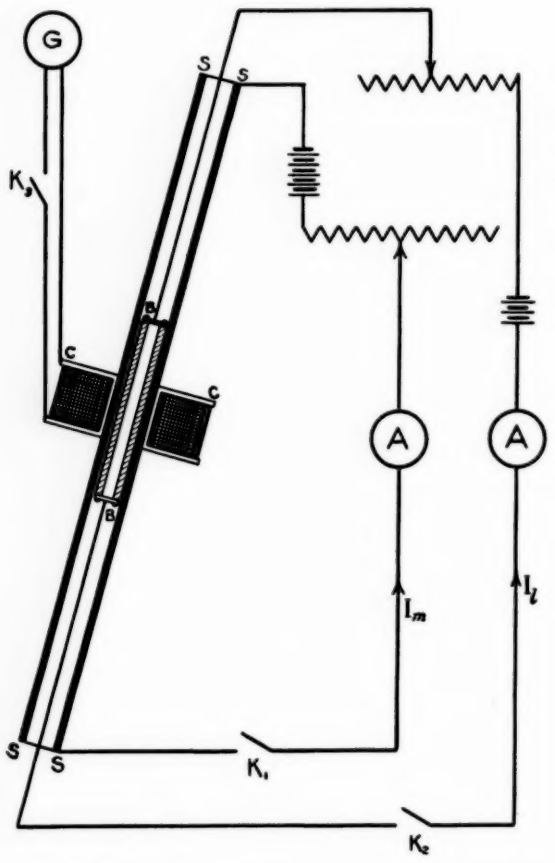

FIG. 1. *Diagram of apparatus.* S.....S—magnetizing solenoid; B.....B—bored out cylinder of Norway iron; C.....C—galvanometer coil.

The difference in the speed with which these two effects take place appears in borderline cases where both are of nearly equal magnitude. The galvanometer starts vigorously in the direction indicating increasing magnetization, but is then deflected with less violence though often farther in the opposite direction. With still larger residual magnetization, the positive throw, indicating an increase, completely dominates the negative throw and increases with increased magnetization and also with an increase in the longitudinal current through the bar.

EXPERIMENTAL ARRANGEMENT

The apparatus used in these experiments has gone through a variety of modifications, but the following arrangement was finally adopted as the most satisfactory one. The bar under investigation is a hollow cylinder about 20 cm long and 2.20 cm diameter with an axial hole 1.2 cm in diameter. In a second exactly similar cylinder cut from the same bar of Norway iron a longitudinal slot about 2 mm wide was cut through the entire length of the cylinder, thus making its section like a nearly closed letter C. This slot was designed to minimize circular magnetization and it resulted in a very marked reduction in the "B effect." The ends of these hollow cylinders were covered with sheet copper caps tightly screwed down and the wires supplying the longitudinal current were soldered to the centers of these caps. In this way it was hoped that the current density throughout the bar's section would be made fairly uniform.

The bar is magnetized by a double layer solenoid of 15 turns per cm having a mean diameter of 3.6 cm and a length of 76 cm. This is set up in line with the earth's field, and Helmholz coils having a diameter of 60 cm are used to neutralize the rather slight influence of terrestrial magnetism on the phenomena under examination. The center of the bar coincides with the center of the solenoid, and a coil 5.5 cm long of 4455 turns of No. 24 wire surrounds the central portion of the solenoid. This coil is connected with a low resistance galvanometer having a sensitivity of 0.35 microvolt per millimeter, but it was used only as a ballistic in all our observations.

Figure 1 shows the essential parts of the apparatus without the Helmholz coils. The commutator switches for reversing the longitudinal current I_l, and the magnetizing current I_m are also omitted.

PROCEDURE

In order to obtain consistent results it was soon found necessary to establish a definite cycle of operations which, if rigidly followed gave galvanometer throws that could be repeated at any time with satisfactory regularity. The procedure adopted was as follows: The iron is first carefully demagnetized. Then I_m is brought up to the value desired by cutting out resistance in its circuit until some point as a in the $B-H$ curve, shown in Fig. 2, has been reached. If the circuit of the magnetizing current is then abruptly broken by opening K_1, the flux decreases from a to some point b on the B axis. Next the galvanometer circuit is closed by means of K_3, and any

desired current I_l is sent through the bar by closing K_2. In those cases when the flux increased, the result is a throw of the galvanometer proportional to *bc*, or when the flux decreased, proportional to *be*. The next step is to open K_3 and close K_1 thus bringing the magnetism back to *d* or *f*. The cycle is then completed by closing K_3 and observing the galvanometer throw when I_l is broken by opening K_2. This throw is proportional to *da* showing a decrease of *B*, or to *af* showing an increase. These values were generally nearly equal to those corresponding to *cb* and *be* but of course in the opposite sense. This cycle may be repeated as many times as desired with only minor changes in the readings.

In our curves we have given changes in the residual flux, $\Delta\phi$, in terms of the galvanometer throws to which they are proportional. But in order to be able to interpret these throws in terms of maxwells we calculated the flux change for several deflections when there was no iron within the solenoid and found that one millimeter on the galvanometer scale corresponds to a change of 0.044 maxwell passing through the coil *CC*.

Before describing a typical series of observations we should point out two important considerations. In all cases in which the residual flux is increased by I_l, the magnetizing current was broken abruptly.[3] If instead I_m is reduced to a very small value by gradually introducing resistance in the circuit, the effect of I_l is invariably to produce a decrease in the residual magnetism. In cases where I_l after an abrupt break caused an increase, the gradual elimination of the magnetizing current was followed by a moderate decrease of residual flux. But in cases where I_l, after an abrupt break, caused a moderate decrease, a slow elimination of I_m was followed by a very large decrease of magnetization produced by I_l. This must mean that an abrupt break brings the point *b* (Fig. 2) to a lower point on the *B* axis than when the current is decreased gradually. To test this peculiarity still further we tried an intermediate procedure of pushing the slider along the drum rheostat as fast as possible from positions of low to high resistance. This gave intermediate results. That is in cases where the magnetism was strongly increased by I_l, after an abrupt break of I_m, the less abrupt decrease of the magnetizing field still resulted in an increase of magnetism, though less than before. In cases where I_l, after an abrupt break caused a decrease, the less abrupt elimination of I_m was followed by a decidedly larger decrease of flux, but not nearly as much as when the field was gradually eliminated.

The other matter to be noted is that there was always a small inductive effect between the I_l circuit and the coil *CC*. This resulted in a reversible throw of the galvanometer on make and break of I_l as has already been mentioned in connection with Villari's experiments. This disturbing throw varied with the orientation of the wires in the galvanometer and longitudinal current circuits, and by careful adjustment could be made as small as two or three millimeters. As this appeared as a constant increase or decrease in the throws caused by changes of flux, we have corrected those readings accordingly.

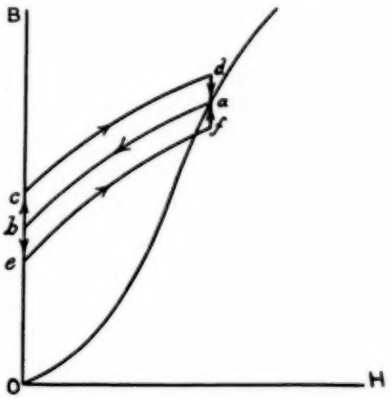

FIG. 2. Magnetic cycles.

RESULTS

Two typical curves obtained with increasing values of the magnetizing field (ignoring the demagnetization by the poles) from 0.0188 oersted created by a current of one milliampere, up to 56.4 oersteds, (3 amperes), and with I_l constant at some value as 0.5 ampere up to 4 amperes (though usually 2) are shown in Fig. 3. Here the axis of ordinates represents $\Delta\phi$, while the axis of abscissas measures the magnetizing field in oersteds. One curve gives the behavior

[3] We have found that in spite of the abrupt break of I_m, the condition of the iron is surprisingly stable. Even when a week elapsed between subjecting the bar to a field of about forty oersteds and the closing of the I_l circuit, the galvanometer indicated the same increase of flux as when there was no appreciable interval.

when K_2 was closed and corresponds to *da* or *fa* in Fig. 2. It is labeled "make." The other labeled "break" represents the behavior when K_2 was opened with I_m flowing, and corresponds to *da* or *fa*. These curves are almost identical in shape though of course reversed. However near the point of reversal, *a*, there is considerable uncertainty due to double throws already mentioned, and its exact position could not be determined with precision. But in general, with I_l at 2

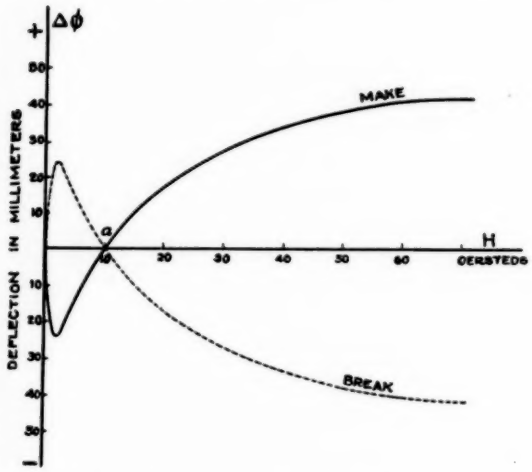

FIG. 3. Typical make and break curves.

amperes, it came when the field was in the neighborhood of 10 oersteds.

The shape of these curves strongly suggests the existence of the two effects we have postulated. For instance the "make" curve, *M*, as shown in Fig. 4, may be decomposed into two other curves *A* and *B* indicating the increasing and decreasing flux caused by the *A* and *B* effects, respectively. This hypothesis was strongly substantiated by observing the effect of a current I_a flowing in a wire placed in the axis of the hollow cylinder. Such an axial current sets up an even stronger circular flux than one flowing in the iron itself, as is found from the following calculation: If we assume the permeability of the iron to be the same when the same current is sent along the axis as when it flows through the iron, and if we suppose the current to be of uniform sectional density, then in the case of the axial current, a familiar calculation gives

$$\phi_a = 2i\mu \log_e \frac{R}{r}, \qquad (1)$$

where R and r are the outer and inner radii of the bored-out cylinder and ϕ_a is the total flux per unit length. In the case of the longitudinal current I_l, the total flux per unit length is given by

$$\phi_l = i\mu\left(1 - \frac{2r^2}{R^2 - r^2} \times \log_e \frac{R}{r}\right). \qquad (2)$$

In our cylinders $r=6$ mm, and $R=11$ mm. Substituting these values and dividing (1) by (2) we obtain $\phi_a/\phi_l = 2.5$ very nearly, Now when H is small (before the *A* effect has really developed) the galvanometer throws indicate roughly twice as great a decrease of magnetization when the current is axial as that produced by a current through the iron. This is near enough the calculated ratio of 2.5 to suggest that the *B* effect tends only to demagnetize the iron.

This demagnetizing effect can be discounted in two ways thus exposing, so to speak, the *A* effect more fully. One way was to send suitably adjusted currents of different values and in opposite directions through the iron and along its axis. Under these circumstances the *B* effect was very much reduced, though we were unable to neutralize it altogether; while the *A* effect gave us larger deflections than when a longitudinal current of the same value acted alone. Apparently the opposite direction of the currents did not alter the *A* effect but by reducing the *B* effect made it appear larger.

The other and even more effective way of reducing the circular flux was to cut a slot in the cylinder as already explained. This greatly increased the reluctance of the bar to circular flux and greatly reduced the *B* effect.

Our latest series of observations was made with the two similar hollow cylinders described above, one slotted, the other not. We made a series of readings for each of four cases beginning with a magnetizing field of less than 0.02 oersted, and ending with about 60 oersteds. The longitudinal and axial currents were both two amperes. These cases are:

No. 1, current through iron, no slot,
No. 2, current through axis, no slot,
No. 3, current through iron, slotted bar,
No. 4, current through axis, slotted bar.

The curves obtained are very illuminating, and

are shown in Fig. 5 with case No. 2 plotted on a scale one-tenth that of the others with respect to the axis of abscissas which is laid off in galvanometer deflections for convenience, although it measures $\Delta\phi$, the change of flux.

If we contrast curves 2 and 4, it becomes evident that the slot has so greatly reduced the very large negative deflections of 2 that the *A* effect is again exhibited. A comparison of curves 1 and 3 also illustrates the effect of the slot though in a lesser degree than when 2 and 4 are compared. The positive galvanometer throws begin earlier and reach higher values in curve 3 than in the other three curves. It should further be noted that in this case the current flows through the iron of a slotted bar, so the circular flux is weaker than in the other cases. At any rate there is no evidence that the *A* effect is stronger in one case than in any other.

We have not yet studied permalloy beyond obtaining a qualitative agreement with the Norway iron. That is, when sufficiently magnetized, there is an increase in the residual flux caused by a current sent through a solid cylinder of the alloy. In the case of a cast iron cylinder bored out and slotted like our other cylinders, we find only a decrease in residual flux as far as we have been able to carry the magnetizing field. However it is significant that whereas an axial current causes a progressively larger decrease in the residual magnetism, as that is raised to higher and higher values, the effect of a current sent through the iron begins to diminish with large values of residual magnetism, and the curve, though still negative, slants upward toward the *H* axis which it seems to be approaching. This suggests the possibility that with sufficiently large magnetizing currents (larger than our coil would carry) the curve might cross the *H* axis, indicating that the *A* effect exists even in cast iron. The nickel bar gave results similar to cast iron, but as yet we have not examined its behavior very thoroughly.

A final experiment was a repetition of what we had roughly measured early in our work. This was a study of the effect of a mechanical jar on residual magnetism. The jar was produced by giving a light tap with a brass rod to the upper end of the bar which had previously been demagnetized both circularly and longitudinally, and then brought up to the desired magnetic intensity by first closing and then opening K_1. The results were surprisingly similar to curve 1, showing first a decrease of residual flux, then, for higher intensities, showing a reversal associated with double throws, and finally quite large deflections indicating the usual increase of residual magnetism. If however the magnetizing current was not broken, when *H* was small, the tap produced a rather large increase in magnetization, while with large values of *H*, beyond about twenty oersteds, the tap caused a decrease. Thus we found more or less complimentary curves like those of Fig. 3.

Discussion of Results

In explaining our observations we have to account for a number of effects which are not easily harmonized. It is necessary to find one or more causes which will simultaneously account for the facts: (a) that a longitudinal current through an iron bar tends to decrease small residual fluxes and increase large ones; (b) that a mechanical jar does the same thing; (c) that a current through the axis causes only a decrease in the residual magnetism, unless the bar is slotted, when results similar to (a) are obtained; (d) that these phenomena depend upon a sudden break in the magnetizing current, and that a more or less gradual decrease in that current tends more or less to result in decreases of the residual flux; (e) that in borderline cases there are

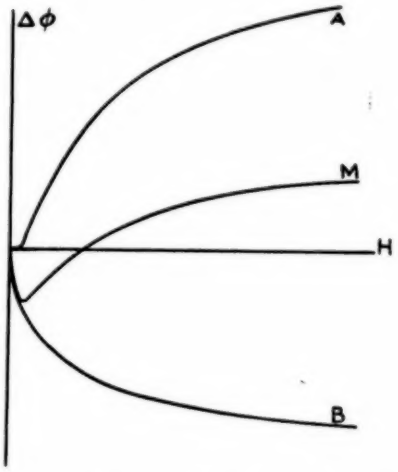

Fig. 4. Proposed decomposition of experimental curve.

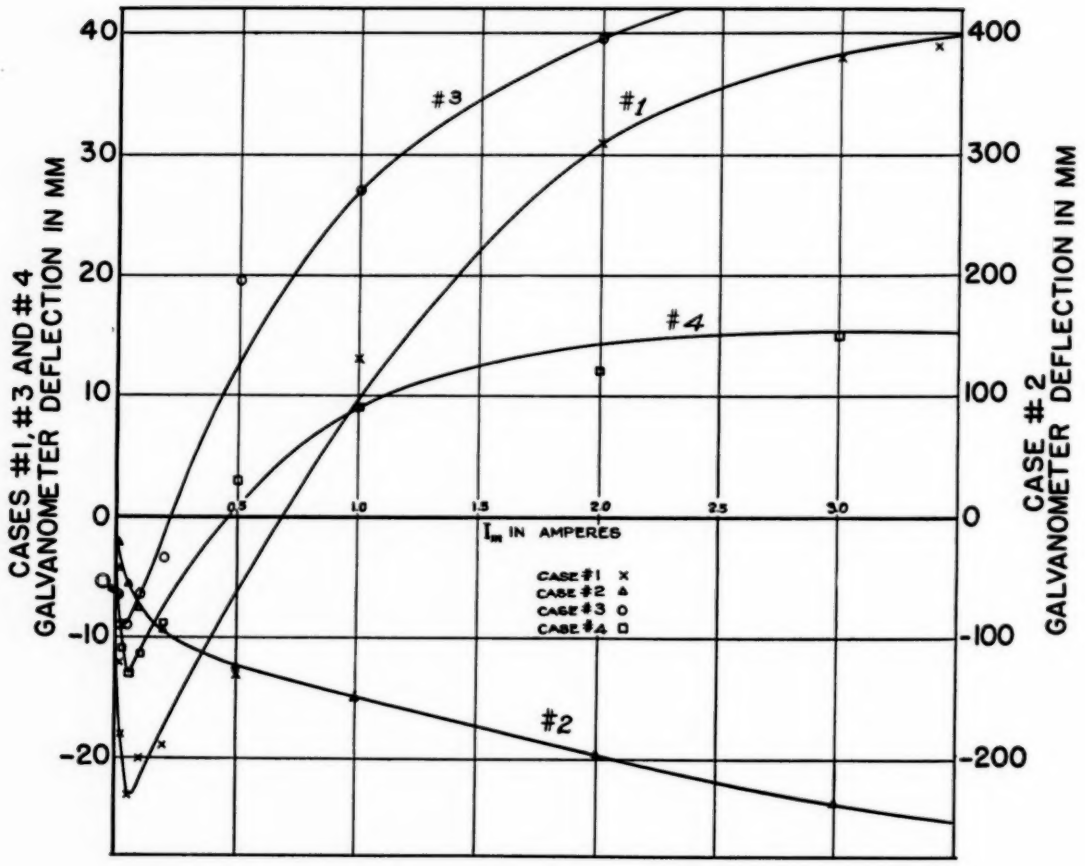

FIG. 5. Four experimental curves, with 2 plotted on a reduced scale of ordinates.

two galvanometer throws, the first being invariably the one indicating an increasing flux.

It might be argued that a circular field applied to a bar which has a residual longitudinal flux would produce a twist in the bar, and that such a twist combined with the circular flux would result in an increase in the residual flux provided the circular flux was small. This effect, based on Wiedeman's experiments, was observed by Nagaoka and Honda[4] in 1902. It amounts to a "Lenz law" reaction to the current which originally created the longitudinal magnetization. But we do not feel that this explanation is satisfactory, because it does not explain the increased flux caused by a mechanical jar after the bar had been carefully deprived of any residual circular flux. Nor does it take into account the fact that slow demagnetization destroys the phenomenon. And further it does not account for the remarkable result of slotting the bar which, if anything, should result in a reduced twist and therefore less of the proposed "Lenz law" reaction, as a result of weakening the circular flux, whereas we found just the opposite to be true.

It seems to us that a possible explanation is that on an abrupt break, the elementary dipoles in swinging away from the position of maximum magnetic intensity overshoot the mark, so to speak, by a kind of momentum, and are then brought back to a more stable position either by a trigger-like action of the mechanical jar, or by the abrupt setting up of a circular flux. This might account for our A effect. Our B effect is also brought about either by a jar or by abruptly setting up a circular field, but it invariably involves a decrease of magnetic intensity. This would be the expected result of a jar, and therefore it seems necessary to suppose that the abrupt creation of a circular field has much the same

[4] H. Nagaoka and K. Honda, Phil. Mag. **4**, 45–72 (1902).

effect, in that it tends to throw the elementary dipoles out of a longitudinal alignment. Thus the same two causes (jar and circular flux) seem to produce two effects, one tending to bring about a more stable alignment of elementary magnets that have overshot the mark, and the other tending to turn them out of that alignment. The fact that in the case of double throws (observed both with mechanical jar and abruptly created circular field) the trigger effect comes first shows that the decrease in longitudinal magnetization takes more time to be produced than the increase caused by a jar or by circular flux after the magnetizing field has been abruptly broken. This seems reasonable, because upsetting an unstable condition should take less time than a more or less permanent rearrangement of the dipoles associated with a decrease of magnetization.

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Internal Diamagnetic Fields*

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In the precise molecular beam experiments of Rabi and his collaborators, it is necessary to know the value at the nucleus of the magnetic field produced by the diamagnetism of the atomic electrons. This has been calculated on the basis of the Fermi-Thomas model, and checked for a number of atoms by use of the available Hartree calculations. The statistical treatment gives for ratio of induced to external field $0.319\times10^{-4}Z^{4/3}$, while the numerical coefficient on the basis of the Hartree model is lower by 19 percent at $Z=19$ and by 12 percent at $Z=80$. The effect is equivalent to a reduction of the nuclear g value by a factor of $(1-0.319\times10^{-4}Z^{4/3})$, and in this form, the correction may be applied in the calculation of hyperfine structure of heavy atoms. The influence of the diamagnetic fields on an orbital electron has also been considered, and it is shown that it is equivalent to a reduction in the g value of an outer s electron by an amount of just the same order of magnitude as the relativistic correction calculated by Margenau.

IN discussing the magnetic properties of solids, it is important to know the value of the magnetic field produced at one atom due to the action of all the *other* atoms. One uses for this some modification of the Lorentz formula.[1] We shall be concerned in this note with the field produced *within* an atom by its own diamagnetic moment when an external field is present. This problem has only arisen because of the very precise molecular beam measurements of Rabi and his collaborators.[2,3]

An external field H (taken along the z axis) may be described by the vector potential

$$\mathbf{A}=\tfrac{1}{2}[\mathbf{H}\times\mathbf{r}] \tag{1}$$

and this induces a diamagnetic current density in the atomic electrons of[4]

$$\mathbf{S}=e\mathbf{A}\rho(\mathbf{r})/mc, \tag{2}$$

where $-e$ is the charge on the electron and $\rho(\mathbf{r})$ is the charge density at $\mathbf{r}$. The induced field is then given by

$$\mathbf{A}'(\mathbf{r})=(e/2mc^2)\int d\mathbf{r}'\rho(\mathbf{r}')[\mathbf{H}\times\mathbf{r}']/|\mathbf{r}-\mathbf{r}'|. \tag{3}$$

When $\rho(\mathbf{r})$ is spherically symmetrical, this may

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] H. Casimir, *Magnetism and Very Low Temperatures* (Cambridge, 1940), p. 56.

[2] P. Kusch, S. Millman, I. I. Rabi, Phys. Rev. **55**, 1176 (1939); P. Kusch, S. Millman, Phys. Rev. **56**, 527 (1939); R. H. Hay, Phys. Rev. **60**, 75 (1941).

[3] P. Kusch, S. Millman, I. I. Rabi, Phys. Rev. **57**, 765 (1940); S. Millman, P. Kusch, Phys. Rev. **58**, 438 (1940); **60**, 91 (1941).

[4] This is most easily derived by considering the induced current in a conducting ring of radius r in the xy plane.

be written as

$$A'(\mathbf{r})=(e/6mc^2)[\mathbf{H}\times\mathbf{r}]\left\{(1/r^3)\int_{r'<r}d\mathbf{r}'r'^2\rho(r')+\int_{r'>r}d\mathbf{r}'\rho(r')/r'\right\}, \quad (4)$$

whence the induced magnetic field along the z direction is

$$H'_z=(eH/2mc^2r^5)(z^2-\tfrac{1}{3}r^2)\int_{r'<r}d\mathbf{r}'r'^2\rho(r')+(eH/3mc^2)\int_{r'>r}d\mathbf{r}'\rho(r')/r'. \quad (5)$$

The induced field at the center of the atom, i.e., that acting on the nuclear spin is just

$$H'(0)_z=(eH/3mc^2)\int_{r'>0}d\mathbf{r}'\rho(r')/r'=(eH/3mc^2)v(0) \quad (6)$$

and depends only on the electrostatic potential $v(0)$ produced at the nucleus by the electrons. One has $v(0)=-Ze(1/r)_{Av}$, and using an effective screening radius $r\sim a_0/Z^{\frac{1}{3}}$, one finds

$$H'(0)_z=-\gamma(e^2/mc^2a_0)Z^{4/3}H=-\gamma\alpha^2Z^{4/3}H, \quad (7)$$

where γ is a number of order unity, a_0 is the Bohr radius, and α is the fine structure constant. The value of γ may be estimated by use of the Fermi-Thomas atom model. According to this[5]

$$V(r)=(Ze/bx)\phi(x) \quad (8)$$

is the total electrostatic potential at a distance from the nucleus $r=bx$, where $b=0.885a_0/Z^{\frac{1}{3}}$, and

$$\phi(x)=1-1.588x+4/3x^{\frac{3}{2}}+\cdots \quad (9)$$

for small x. The electronic contribution to the potential at the nucleus is then

$$v(0)=-1.588Ze/b,$$

whence γ has the value $(1.588/0.885)/3=0.598$ and

$$H'(0)_z=-0.319\times10^{-4}Z^{4/3}H. \quad (10)$$

[5] E. Condon and G. Shortley, *Theory of Atomic Spectra* (Cambridge, 1935), p. 336; L. Brillouin, *L'Atome de Thomas-Fermi* (Hermann, Paris, 1934).

The correction in magnetic field acting on the nucleus must also be applied to the field produced by an orbital electron when one calculates hyperfine structure. It is easy to show that this case may be combined with that of an external field by keeping the applied field constant, and changing the nuclear g factor to $g(1-0.319\times10^{-4}Z^{4/3})$, except for some negligible errors due to the field produced by the outermost electrons.

These simple formulae can be improved in any particular case by use of the Hartree model. For a number of atoms, values of $v(0)$ have been given explicitly by Hartree and others. Thus for[6] $_{19}$K, $_{20}$Ca, $_{26}$Fe, $_{29}$Cu, $_{37}$Rb, $_{55}$Cs, $_{74}$W, $_{80}$Hg, one finds that the number 0.319 in Eq. (10) should be replaced by the numbers 0.259, 0.259, 0.263, 0.268, 0.270, 0.274, 0.277, 0.280, respectively. Thus it is seen that for these elements, the Fermi-Thomas $Z^{4/3}$ law is checked very well, although the numerical coefficient is too high by an amount varying smoothly from 19 to 12 percent.

In the radiofrequency experiments with atoms,[3] one has beside the nuclear spin, an orbital electron usually in a $^2S_{\frac{1}{2}}$ state. We shall now discuss the effect of the induced field on this outer electron. It is seen from Eq. (5) that the induced field H'_z at any distance r may be divided into two parts. One is due to electrons inside the sphere of radius r, the other due to electrons outside of the sphere. The first contribution varies like the second Legendre polynomial $P_2(\cos\theta)$ with angle, and averages to zero in its effect on an s electron. The second contribution does not vary with angle, but it is small for an outer electron which does not penetrate much into the core. We can estimate the effective induced field for such an electron as follows. We must average

$$H''(r)_z=(eH/3mc^2)\int_{r'>r}d\mathbf{r}'\rho(r')/r' \quad (11)$$

over the orbit of the outer electron. With Poisson's equation

$$\frac{d^2V}{dr^2}+\frac{2}{r}\frac{dV}{dr}=-4\pi\rho(r), \quad (12)$$

[6] The references used are given in F. Seitz, *Modern Theory of Solids* (McGraw-Hill, 1940), p. 251, except for the case of Fe which was obtained from M. Manning and L. Goldberg, Phys. Rev. **53**, 662 (1938).

the integral, which is just the potential due to the electrons of the core beyond r, can be expressed as

$$\int = V(r)+r(dV/dr), \tag{13}$$

where $V(r)$ is the potential acting on the orbital electron. If we write $V(r)=eZ(r)/r$, this becomes $edZ(r)/dr$, so that the effective magnetic field is

$$(H''_z)_{Av}=(e^2/3mc^2)H(dZ(r)/dr)_{Av}. \tag{14}$$

By applying the virial theorem to a potential of the above form, one finds

$$e^2(dZ(r)/dr)_{Av}=W-T, \tag{15}$$

where W is the binding energy of the orbital electron and T is its average kinetic energy. The two quantities are of course equal for a pure coulomb field, but the average kinetic energy is larger than the binding energy for an atomic field because of the penetration of the orbital electron into regions of the core where the effective Z is larger than unity. A very simple, although rough way to estimate the difference $T-W$ is the following: For orbits with small penetration, one can expand $Z(r)$ as a power series in inverse powers of r. For large r only, one could write

$$Z(r)=1+\zeta(a_0/r), \text{ where } \zeta \text{ is a constant.}$$

Then

$$T-W=\zeta a_0 e^2(1/r^2)_{Av}. \tag{16}$$

Now the binding energy of the electron is equal to the hydrogenic value $W_0=e^2/(2n^2a_0)$ increased by

$$\zeta a_0 e^2(1/r^2)_{Av}.$$

Hence $T-W\backsimeq W-W_0$, and we can express our results simply in terms of the excess binding energy of the electron over the hydrogenic value, so that

$$(H''_z)_{Av}\backsimeq -(H/3mc^2)(W-W_0). \tag{17}$$

This induced field is always of the order 10^{-5} of the applied field, and hence does not affect the discussion of the radiofrequency experiments in their present state of precision, although this can probably be increased.

It will be noticed that the atomic electron behaves as if its g value were reduced from the value 2 to the value

$$g=2(1-(T-W)/3mc^2). \tag{18}$$

This is of the same order, but distinct from the relativistic change in the g factor discussed by Margenau,[7] who found

$$g=2[1-\tfrac{2}{3}(T/mc^2)]. \tag{19}$$

His effect arises because of the change in the magnetic moment of an electron due to its motion in a fixed potential field, while we have considered the fact that the potential field itself is changed by the presence of an external magnetic field, at least in the present case where this field is produced by electronic charges. Both corrections must be considered in order to obtain the effective g value of an s electron.

These calculations were suggested to me by members of the molecular beam laboratory of Columbia University. I am indebted to them for helpful discussions.

[7] H. Margenau, Phys. Rev. **57**, 383 (1940). It has been shown by M. Phillips, Phys. Rev. **60**, 100 (1941) that interconfiguration interactions do not affect the g value of an alkali atom in the ground state.

On the Thermal Conductivity of Dielectrics

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As is well known, Peierls and Debye found that, if $T \gg \theta$ (T is the temperature, θ—the Debye temperature), the thermal conductivity κ of dielectrics varies inversely to the temperature. However, this turns out to be true only for dielectrics obeying the definite law of sound velocity dispersion and the definite law of the dependence of sound velocity on the direction. For all other dielectrics at $T \gg \theta$, κ is inversely proportional to T^2. This results from investigation of the free path of long elastic waves.

PEIERLS[1] and Debye[2] have found the dependence of thermal conductivity κ of dielectrics on the temperature for the cases in which T is very much greater than θ the Debye temperature. In order to clarify the problem we shall consider the situation which arises in the body with no dispersion of sound and with isotropic sound velocity.

As is known,[3] the absorption coefficient of the transversal sound (i.e., of transversal phonons) varies as ω, ω being a circular frequency. It is easily found that at $T \gg \theta$ the phonon free path l is of the form:

$$l \approx \alpha(Ms^2/KT)(K\theta/\hbar\omega), \quad (T \gg \theta). \tag{1}$$

Here M is the mass of the elementary cell, K the Boltzmann constant, s the velocity of sound, α the lattice constant. Absorption coefficient of longitudinal sound depends on the existence of the possibility of the absorption of a long wave-length longitudinal phonon by short wave-length phonons. From the conservation laws it follows, that

$$\mathbf{f}+\mathbf{F}=\mathbf{F}'; \quad \omega(\mathbf{f})+\omega(\mathbf{F})=\omega(\mathbf{f}+\mathbf{F}). \tag{2}$$

Here $\mathbf{f}$ stands for the wave vector of a long wave-length longitudinal phonon, $\mathbf{F}$ for wave vector of a Debye short wave-length phonon. We get:

$$\omega(\mathbf{f})=\mathbf{f}\frac{\partial\omega}{\partial\mathbf{F}}; \quad s_{\text{long}} f = \mathbf{f}\mathbf{V}_{\mathbf{F}}. \tag{3}$$

s_{long} is a longitudinal sound velocity, $V_{\mathbf{F}}$ is the group velocity of a Debye phonon.

If, as for the body under consideration, $s_{\text{long}} \geqslant V_{\mathbf{F}}$, the process (2) is impossible. For bodies having such a dispersion law and an anisotropic sound velocity, the absorbtion of a long wave-length longitudinal phonon is only possible if it splits into two small transversal phonons or into one small transversal and one small longitudinal phonon. The absorption coefficient turns out to be proportional to ω^4 (in distinction to ω^5, as was obtained by Slonimsky[4]). The free path l^{III} may be written, if the order of the value is only concerned, as follows:

$$l^{\text{III}} \approx \alpha(Ms^2/KT)(K\theta/\hbar\omega)^4. \tag{4}$$

Moreover, the absorption of longitudinal phonons due to collisions involving four phonons must be taken into account as well. The corresponding free path is of the form:

$$l^{\text{IV}} \approx \alpha(Ms^2/KT)^2(K\theta/\hbar\omega)^2. \tag{5}$$

Equations (4) and (5) give equal quantities at the frequency ω_0, at which

$$\hbar\omega_0 = K\theta(KT/Ms^2)^{\frac{1}{2}}, \quad (T \gg \theta). \tag{6}$$

It is evident that in these conditions the heat is transferred by small longitudinal phonons because they have enormous free paths.

The thermal conductivity κ equals:

$$\kappa \approx \int C_\omega l_\omega V_{\mathbf{F}} \frac{\omega^2 d\omega dO}{(2\pi s)^3}, \quad dO = \sin\vartheta d\vartheta d\varphi. \tag{7}$$

[1] R. Peierls, Ann. d. Physik **3**, 1055 (1929).
[2] P. Debye, *Vorträge uber die Kinetische Theorie* etc., s. 43 (Teubner, 1914).
[3] L. Landau and G. Rumer, Sowjetunion Physik. Zeits. **11**, 18 (1937).
[4] Slonimsky, J. Exper. and Theor. Phys. (Russian) **7**, 1457 (1937).

Here C_ω is the specific heat of a given phonon. Because small frequencies alone are of any importance, C_ω may be put equal to K. Introducing Eq. (4) into (7) we get after integration up to ω_0, this limit resulting from Eq. (6):

$$\kappa \approx \alpha K s \frac{Ms^2}{KT}\left(\frac{K\theta}{\hbar s}\right)^3 \frac{K\theta}{\hbar\omega_0}\frac{4\pi}{(2\pi)^3}$$

$$= \alpha K s \left(\frac{Ms^2}{KT}\right)^{\frac{1}{2}}\left(\frac{K\theta}{\hbar s}\right)^3 \frac{1}{2\pi^2}$$

$$= \alpha K s \left(\frac{Ms^2}{KT}\right)^{\frac{1}{2}} \frac{1}{2\pi^2\alpha^3}\left(\frac{K\theta\alpha}{\hbar s}\right)^3.$$

Let us designate $1/\alpha^3$ by n, which is the quantity of the same order as the total number of atoms (or molecules) per cc, and use the relation:

$$K\theta \sim (\hbar s/\alpha)(2\pi^2)^{\frac{1}{3}}.$$

Then

$$\kappa \sim nKs\alpha(Ms^2/KT)^{\frac{1}{2}}, \quad (T \gg \theta).$$

Thus for the bodies, for which $s_{\max} \gtrsim V_F$, $s_{\max}$ being the velocity of the oscillations having the greatest velocity, the thermal conductivity at high temperatures varies as $T^{-\frac{1}{2}}$, in distinction to the results of Peierls[1] and Debye.[2]

If $s_{\max} < V_F$, the difference with respect to the absorption between "longitudinal" and "transversal" sound vanishes and the result obtained by Peierls[1] and Debye[2] remains to be true.

At low temperatures ($T \ll \theta$), according to detailed calculations, only the admixtures, the reflection from boundaries of small crystals and the collisions of triples of phonons are essential for the evaluation of κ. In distinction to the case treated by Peierls,[5] here the finite value of thermal conductivity cannot be obtained if we consider only the scattering of phonon on the atoms of admixture and the collision of triples of phonons, because in both effects the free path varies as ω^{-4}. The finite value of thermal conductivity can be obtained only if the reflection from small crystal boundaries is taken into account. The resulting expression for κ turns out to be inverse to $L^{\frac{1}{2}}$, L being the linear dimension of the crystal. Therefore, at low temperatures the thermal conductivity, as found experimentally, depends (although not strong) on the shape of the crystal. This holds even if the phonon free path for the frequency of the order $KT/\hbar$ is much less than the crystal dimensions. If the temperature is decreased and becomes less than the Debye temperature, thermal conductivity at first increases inversely to $T^{\frac{1}{2}}$, but finally it does not depend on temperature at low temperatures for which the waves with $\omega = KT/\hbar$ have the free path of the same order, as the crystal dimensions. Further decrease of temperature as is known, leads to variation of κ proportional to T^3.[6,7]

The temperature range in which κ does not change at all is especially wide for the diamond because of its high value of Debye temperature. This result explains the experimental data concerning the thermal conductivity of diamond,[8,9] according to which data κ reveals no noticeable change in the temperature range from 24 to 343°.

Detailed calculations have been published in *Journal of Physics* [**4**, 259 (1941)]. In the same publication the calculations involving the region of low temperatures are to appear shortly.

[5] R. Peierls, Ann. d. Physik **3**, 1097 (1929).

[6] W. J. de Haas and T. Biermasz, Physica **5**, 619 (1938).
[7] H. B. G. Casimir, Physica **5**, 495 (1938).
[8] Eucken, Physik. Zeits. **12**, 1055 (1911).
[9] W. J. de Haas and T. Biermasz, Physica **5**, 47 (1938).

On the Distribution of Lattice Vibrations of the KCl Crystal

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The distribution of characteristic vibrations of the KCl crystal has been calculated following Born, v. Kármán and Blackman under the assumption of both electrostatic and repulsive forces between the ions, the latter calculated for the 18 nearest neighbors from the elastic constants and the residual ray frequency. Application of this distribution has been made to the evaluation of the specific heat at low temperatures.

INTRODUCTION

TO give detailed explanation of many properties of crystals, e.g., temperature dependence of the specific heat and the diffuse scattering of x-rays, it is desirable to know the equation of motion and the distribution of characteristic vibrations. These can be calculated from the lattice configuration and the forces between the atoms. The latter have often been calculated by means of the elastic constants, but this method allows the determination of only a few force constants and is therefore only useful as long as short range forces are considered. This method is hence applicable to atomic crystals, such as the tungsten crystal, which has been treated in detail by Fine.[1] In the case of ion crystals it is necessary to notice that the electrostatic forces act also between ions of greater separation and have to be considered in a different way. The method of considering the electrostatic forces separately has been used by Lyddane and Herzfeld[2] for calculation on NaCl, more recently by Kellermann[3] for the same crystal. Ljungquist[4] and Foldy[5] use this method on the KCl crystal. Lyddane, Herzfeld and Foldy use theoretical statements for the short range forces. Kellermann calculated the force constants between 6, Ljungquist between 18 nearest neighbors using the experimental values of the elastic constants.

* Now at the University of Chicago.
[1] P. C. Fine, Phys. Rev. **56**, 355 (1939).
[2] R. H. Lyddane and K. F. Herzfeld, Phys. Rev. **54**, 846 (1938).
[3] E. W. Kellermann, Phil. Trans. Roy. Soc. **238**, 513 (1940).
[4] S. Ljungquist, Uppsala. To be published.
[5] L. L. Foldy, Phys. Rev. **60**, 64 (1941).

THE FREQUENCY SPECTRUM‡

To calculate the distribution function for the simplest cubic crystal, the KCl crystal, the masses of the ions may be assumed to be equal and, under the assumption of equal forces (except for the difference in sign of the charge) between the ions, the crystal may be considered as a simple cubic lattice. In order to find the number of characteristic vibrations in given frequency intervals it is necessary to consider the equation of motion of the ions, which may be taken to be oscillating as a whole. One obtains these equations from the general equation of motion in the following way: the gradient of the potential energy of the ions, expanded in a power series of the displacement of the particles, is substituted for the force and the motion is taken to be oscillatory. If one assumes a plane wave solution, the displacement of the ions, whose rest position is characterized by the vector $\boldsymbol{l}$ with integral components, may be described as follows:

$$\boldsymbol{u}_l = \boldsymbol{U}e^{-i\omega t}\exp[i(\boldsymbol{\phi l})]. \qquad (1)$$

$\boldsymbol{U}$ indicates the amplitude of the oscillations with frequency $\omega = 2\pi\nu$, $\boldsymbol{\phi}$ is a vector in the direction of wave propagation of the magnitude $2\pi a/\lambda$, a is the distance between nearest lattice points and λ the wave-length. The vector $\boldsymbol{\phi}$, whose components φ_i are usually called phase components, characterizes thus both wave-length and direction of the waves. To be free from the boundary conditions of the crystal it is convenient, following Born, to consider a "cyclic lattice;" that is an infinite lattice which repeats the finite lattice inclusive of its motion periodically in each direc-

‡ For the formulae used see reference 11.

tion. If the considered finite lattice has n elementary cells in each direction, each cell containing one particle, the condition of periodicity of motion makes $n\varphi_i$ an integral multiple of 2π. Since the wave function has physical significance only at the lattice points the φ_i may be restricted to $-\pi \leq \varphi_i \leq \pi$. The values φ_i ($\varphi_i = 2\pi p_i/n$) build a cubic lattice with the lattice constant $2\pi/n$ and the edge length 2π; this is the so-called phase cube. The number of lattice points in a volume element $(d\varphi)$, or the number of characteristic vibrations which is proportional to this number is given by

$$dn = 3(n/2\pi)^3(d\varphi) \tag{2}$$

since to each point of the phase cube three characteristic vibrations correspond. The integration of expression (2) gives $3n^3$, the number of degrees of freedom. In order to find from the number of vibrations in the volume element of the phase cube the distribution of lattice vibrations along the frequency scale the relation between frequency and phase components must be found. One obtains this relation from the condition that the equations of motion give the ratios between the amplitude components, so that the determinant of the equations of motion vanishes.

With the assumed oscillation (1) the equations of motion turn out to be:

$$\begin{aligned} (A_{11}+m\omega^2)U_1 + A_{12}U_2 + A_{13}U_3 &= 0, \\ A_{21}U_1 + (A_{22}+m\omega^2)U_2 + A_{23}U_3 &= 0, \\ A_{31}U_1 + A_{32}U_2 + (A_{33}+m\omega^2)U_3 &= 0. \end{aligned} \tag{3}$$

The coefficients $A_{ik}(\boldsymbol{\phi})$ are given from the derivatives of the potential energy of the ions in direction of the i and k coordinates by

$$A_{ik}(\boldsymbol{\phi}) = \sum_l{}' \psi_{ik}^l[\exp(-i(l\boldsymbol{\phi}))-1] = A_{ik}^e + A_{ik}^r. \tag{4}$$

These coefficients can be divided into two parts, one due to the electrostatic forces (A_{ik}^e) and the other to the repulsive forces (A_{ik}^r).

The method given by Ewald[6] allows the calculation of the electrostatic parts. Following Waller[7]* one obtains:

$$A_{ik}^e(\boldsymbol{\phi}) = -\frac{4\pi e^2}{a^3}\sum_N \left\{ \frac{(N_i+\mu_i)(N_k+\mu_k)}{\sum_{m=1}^{3}(N_m+\mu_m)^2} \exp\left[-\frac{\pi^2}{4\eta^2}\sum_{m=1}^{3}(N_m+\mu_m)^2\right] - \frac{N_iN_k}{\sum_{m=1}^{3}N_m^2}\exp\left[-\frac{\pi^2}{4\eta^2}\sum_{m=1}^{3}N_m^2\right]\right\}$$

$$+\frac{e^2}{a^3}\sum_l{}'(-1)^{l_1+l_2+l_3}[\exp(i(\boldsymbol{\phi}\boldsymbol{l}))-1]\frac{1}{l^3}\left\{\left(\frac{3l_il_k}{l^2}-\delta_{ik}\right)\left(1-G(\eta l)-\frac{G''(\eta l)}{2}\right)-\eta^2 l_il_kG''(\eta l)\right\}. \tag{5}$$

In these equations $\sum_N$ is a sum over all triplets of odd numbers, and $\sum'_l$ a sum over all triplets of integral numbers except (0, 0, 0), $G(x)$ is the error function

$$G(x) = \frac{2}{\sqrt{\pi}}\int^x \exp(-\alpha^2)d\alpha$$

and $G''(x)$ its second derivative. The length of the vector $\boldsymbol{l}$ is l and $\mu_i = \varphi_i/\pi$. By assuming a proper value for the constant η it is possible to find sufficiently convergent series of both types. The calculations have been carried out with $\eta = 1$ which give the higher number of terms in the more convenient second sum. The coefficients have been checked by means of the Laplace equation or by using different values for η. To check the method the electrostatic parts of the elastic constants have been calculated and compared with the sums given by Born.

The coefficients A_{ik}^r have been calculated by following the method of Born, v. Kármán,[8] and Blackman.[9] For this purpose the force constants P and Q have been used which Ljungquist[4] obtained from the experimental values of the

[6] P. Ewald, Ann. d. Physik **64**, 253 (1921).

[7] I am much indebted to Professor I. Waller for giving me these unpublished formulae.

* At the same time Kellermann calculated in England the coefficients for the NaCl crystal. The coefficients given above may be obtained from his formulae as the special case for equal ion masses.

[8] M. Born, Th. v. Kármán, Physik. Zeits. **13**, 297 (1912); **14**, 15, 65 (1913).

[9] M. Blackman, Proc. Roy. Soc. **A148**, 365, 384 (1935); **A159**, 416 (1937).

elastic constants (c_{11} and c_{12}) given by Försterling,[10] from the residual ray frequency ($\lambda_0 = 70.7 \times 10^{-4}$ cm) and from the equilibrium condition after splitting these values in electrostatic parts[11] and the parts due to the repulsive forces.

$$A^{r}_{ii}(\boldsymbol{\phi}) = -2(Q_{12}a^2 + P_{12})(1-\cos\varphi_i) - 2P_{12}(2-\cos\varphi_k-\cos\varphi_l) - 4(Q_{11}a^2+P_{11})(2-\cos\varphi_i\cos\varphi_k - \cos\varphi_i\cos\varphi_l) - 4P_{11}(1-\cos\varphi_k\cos\varphi_l), \quad (6)$$

$$A^{r}_{ik}(\boldsymbol{\phi}) = -4Q_{11}a^2 \sin\varphi_i \sin\varphi_k. \quad i \neq k \neq l \neq i.$$

The numerical values of the constants are:

$$P_{11} = -0.0469 \times 10^3; \quad P_{12} = -1.992 \times 10^3;$$

$$Q_{11} = -0.0315 \times 10^{19}; \quad Q_{12} = 2.5218 \times 10^{19}.$$

TABLE I. *Values of electrostatic parts of coefficients* A_{ik}.

μ_1	μ_2	μ_3	A^{e}_{11} $\times 10^{-3}$	A^{e}_{22} $\times 10^{-3}$	A^{e}_{33} $\times 10^{-3}$	A^{e}_{12} $\times 10^{-3}$	A^{e}_{13} $\times 10^{-3}$	A^{e}_{23} $\times 10^{-3}$	
0	0	$\frac{1}{4}$	− 2.82	− 2.82	+ 5.63	0	0	0	
0	0	$\frac{1}{2}$	− 9.78	− 9.78	+19.55	0	0	0	
0	0	$\frac{3}{4}$	−16.97	−16.97	+33.93	0	0	0	
0	0	1	−20.01	−20.01	+40.03	0	0	0	
0	$\frac{1}{4}$	$\frac{1}{4}$	− 6.12	+ 3.06	+ 3.06	0	0	− 2.69	
0	$\frac{1}{4}$	$\frac{1}{2}$	−14.34	− 3.35	+17.68	0	0	− 4.02	
0	$\frac{1}{4}$	$\frac{3}{4}$	−22.97	− 9.98	+32.95	0	0	− 2.99	
0	$\frac{1}{4}$	1	−26.66	−12.83	+39.48	0	0	0	
0	$\frac{1}{2}$	$\frac{1}{2}$	−25.95	+12.98	+12.98	0	0	− 6.00	
0	$\frac{1}{2}$	$\frac{3}{4}$	−38.51	+ 8.03	+30.49	0	0	− 4.52	
0	$\frac{1}{2}$	1	−44.03	+ 5.88	+38.14	0	0	0	
0	$\frac{3}{4}$	$\frac{3}{4}$	−55.83	+27.92	+27.92	0	0	− 3.43	
0	$\frac{3}{4}$	1	−63.59	+26.81	+36.79	0	0	0	
0	1	1	−72.44	+36.22	+36.22	0	0	0	
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0	0	− 3.35	− 3.35	− 3.35	
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	− 7.70	− 7.70	+15.40	− 5.10	− 5.08	− 5.08	
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	−15.89	−15.89	+31.78	− 7.17	− 3.87	− 3.87	
$\frac{1}{4}$	$\frac{1}{4}$	1	−19.45	−19.45	+38.90	− 8.14	0	0	
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	−19.07	+ 9.54	+ 9.54	− 8.11	− 8.11	− 7.88	
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	−31.86	+ 3.06	+28.80	−11.90	− 6.49	− 6.14	
$\frac{1}{4}$	$\frac{1}{2}$	1	−37.66	+ 0.16	+37.50	−13.76	0	0	
$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	−50.95	+25.48	+25.48	− 9.73	− 9.73	− 4.94	
$\frac{1}{4}$	$\frac{3}{4}$	1	−60.07	+23.98	+36.09	−11.84	0	0	
$\frac{1}{4}$	1	1	−71.03	+35.52	+35.52	0	0	0	
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	−13.52	−13.52	−13.52	
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}$	−11.97	−11.97	+23.96	−21.54	−11.53	−11.53	
$\frac{1}{2}$	$\frac{1}{2}$	1	−17.98	−17.98	+35.96	−25.88	0	0	
$\frac{1}{2}$	$\frac{3}{4}$	$\frac{3}{4}$	−34.49	+17.25	+17.25	−20.64	−20.64	−10.89	
$\frac{1}{2}$	$\frac{3}{4}$	1	−47.87	+13.46	+34.42	−26.42	0	0	
$\frac{1}{2}$	1	1	−67.58	+33.79	+33.79	0	0	0	
$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	0	0	0	−25.82	−25.82	−25.82	
$\frac{3}{4}$	$\frac{3}{4}$	1	−16.36	−16.36	+32.74	−41.23	0	0	
$\frac{3}{4}$	1	1	−64.09	+32.05	+32.05	0	0	0	
			−62.66	+31.33	+31.33	0	0	0	(x,1,1)*
1	1	1	−15.67	−15.67	+31.33	−46.99	0	0	(x,x,1)
			0	0	0	−31.33	−31.33	−31.33	(x,x,x)

* Indicates the direction in which this point is approached.

[10] K. Försterling, Zeits. f. Physik **2**, 172 (1920).

[11] M. Born and M. Göppert-Mayer, *Handbuch der Physik* Vol. 24–2 (1934); M. Born, *Enzyklopädie d. Math. Wiss.* Vol. 5–3 (1923).

The coefficients A_{ik} are uniquely determined at all points of the phase cube except at the point (π, π, π). Terms of the magnitude of the reciprocal vacuum wave-length have been neglected in comparison to terms of at least the magnitude of the reciprocal lattice constant, which means we have neglected the retardation. At the point (π, π, π) these latter terms vanish and the coefficients A^{e}_{ik} depend on the direction from which this point is approached. At this point only the retardation cannot be disregarded but the distribution of vibrations is not changed by the value at this cornerpoint. Even at this point the solution of the secular equation gives a distinct set of frequencies.‡

Because the coefficients depend only on the magnitude of the phase components it is sufficient to carry out the calculations for the positive octant of the phase cube. As a permutation of the φ_i gives the same frequency triplets it is sufficient to calculate the frequencies at 35 points in order to know them at all points differing by $\frac{1}{4}\pi$ in the phase coordinates. Because of the symmetry of the coefficients all but one of the secular equations split up into equations of lower degree.

The numerical values of the coefficients and the frequencies are collected in Tables I–III. Table I gives the electrostatic parts of the coefficients calculated with the factor $e^2/a^3 = 7.479 \times 10^3$. Table II contains the coefficients A^{r}_{ik} and Table III gives the frequencies.

Born, v. Kármán, and Blackman obtain with coefficients analogous to (6) at the point (π, π, π) of the phase cube three equal frequencies corresponding to the residual ray frequency. Considering the long range Coulomb forces one obtains two vibrations with residual ray frequency and one of almost double this frequency ($\lambda_0 = 39.9 \times 10^{-4}$ cm).

The three frequencies at each point of the phase cube have been arranged in three branches of vibrations, one containing the highest, one the medium and one the lowest frequencies at each point. It was possible in this way to combine all frequencies by three smooth surfaces of the

‡ For more detailed discussion of the effect of retardation see reference 3, and J. H. Thompson, Proc. Roy. Soc. **A149**, 487 (1935).

TABLE II. *Values of repulsive parts of coefficients* A_{ik}.

μ_1	μ_2	μ_3	A_{11} $\times 10^{-3}$	A_{22} $\times 10^{-3}$	A_{33} $\times 10^{-3}$	A_{12} $\times 10^{-3}$	A_{13} $\times 10^{-3}$	A_{23} $\times 10^{-3}$
0	0	$\frac{1}{4}$	+ 1.64	+ 1.64	−12.53	0	0	0
0	0	$\frac{1}{2}$	+ 5.60	+ 5.60	−42.76	0	0	0
0	0	$\frac{3}{4}$	+ 9.56	+ 9.56	−73.00	0	0	0
0	0	1	+11.20	+11.20	−85.53	0	0	0
0	$\frac{1}{4}$	$\frac{1}{4}$	+ 3.26	−11.01	−11.01	0	0	+0.62
0	$\frac{1}{4}$	$\frac{1}{2}$	+ 7.18	− 7.34	−41.54	0	0	+0.88
0	$\frac{1}{4}$	$\frac{3}{4}$	+11.10	− 3.68	−72.08	0	0	+0.62
0	$\frac{1}{4}$	1	+12.73	− 2.16	−84.72	0	0	0
0	$\frac{1}{2}$	$\frac{1}{2}$	+11.01	−38.59	−38.59	0	0	+1.24
0	$\frac{1}{2}$	$\frac{3}{4}$	+14.84	−35.64	−69.84	0	0	+0.88
0	$\frac{1}{2}$	1	+16.42	−34.42	−82.78	0	0	0
0	$\frac{3}{4}$	$\frac{3}{4}$	+18.57	−67.60	−67.60	0	0	+0.62
0	$\frac{3}{4}$	1	+20.11	−66.68	−80.84	0	0	0
0	1	1	+21.64	−80.04	−80.04	0	0	0
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	− 9.51	− 9.51	− 9.51	+0.62	+0.62	+0.62
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	− 5.88	− 5.88	−40.34	+0.62	+0.88	+0.88
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	− 2.26	− 2.26	−71.16	+0.62	+0.62	+0.62
$\frac{1}{4}$	$\frac{1}{4}$	1	− 0.76	− 0.76	−83.94	+0.62	0	0
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	− 2.35	−37.43	−37.43	+0.88	+0.88	+1.24
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	+ 1.18	−34.52	−68.97	+0.88	+0.62	+0.88
$\frac{1}{4}$	$\frac{1}{2}$	1	+ 2.64	−33.31	−82.03	+0.88	0	0
$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	+ 4.62	−66.77	−66.77	+0.62	+0.62	+0.62
$\frac{1}{4}$	$\frac{3}{4}$	1	+ 6.03	−65.86	−80.13	+0.62	0	0
$\frac{1}{4}$	1	1	+ 7.45	−79.35	−79.35	0	0	0
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	−34.61	−34.61	−34.61	+1.24	+1.24	+1.24
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}$	−31.79	−31.79	−66.86	+1.24	+0.88	+0.88
$\frac{1}{2}$	$\frac{1}{2}$	1	−30.62	−30.62	−80.23	+1.24	0	0
$\frac{1}{2}$	$\frac{3}{4}$	$\frac{3}{4}$	−29.07	−64.76	−64.76	+0.88	+0.88	+0.62
$\frac{1}{2}$	$\frac{3}{4}$	1	−27.94	−63.89	−78.42	+0.88	0	0
$\frac{1}{2}$	1	1	−26.83	−77.67	−77.67	0	0	0
$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	−62.75	−62.75	−62.75	+0.62	+0.62	+0.62
$\frac{3}{4}$	$\frac{3}{4}$	1	−61.92	−61.92	−76.70	+0.62	0	0
$\frac{3}{4}$	1	1	−61.10	−75.99	−75.99	0	0	0
1	1	1	−75.30	−75.30	−75.30	0	0	0

TABLE III. *Values of the frequencies.*

μ_1	μ_2	μ_3	$\omega_1 \times 10^{-13}$	$\omega_2 \times 10^{-13}$	$\omega_3 \times 10^{-13}$
0	0	$\frac{1}{4}$	1.06	0.44	0.44
0	0	$\frac{1}{2}$	1.94	0.82	0.82
0	0	$\frac{3}{4}$	2.51	1.09	1.09
0	0	1	2.71	1.19	1.19
0	$\frac{1}{4}$	$\frac{1}{4}$	1.27	0.97	0.68
0	$\frac{1}{4}$	$\frac{1}{2}$	1.99	1.27	1.08
0	$\frac{1}{4}$	$\frac{3}{4}$	2.52	1.47	1.39
0	$\frac{1}{4}$	1	2.70	1.56	1.50
0	$\frac{1}{2}$	$\frac{1}{2}$	2.21	1.84	1.55
0	$\frac{1}{2}$	$\frac{3}{4}$	2.55	2.07	1.96
0	$\frac{1}{2}$	1	2.69	2.15	2.11
0	$\frac{3}{4}$	$\frac{3}{4}$	2.62	2.45	2.44
0	$\frac{3}{4}$	1	2.67	2.65	2.54
0	1	1	2.86	2.66	2.66
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1.55	1.05	1.05
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	2.14	1.54	1.21
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	2.56	1.94	1.36
$\frac{1}{4}$	$\frac{1}{4}$	1	2.70	2.12	1.43
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	2.55	1.85	1.60
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	2.82	2.32	1.80
$\frac{1}{4}$	$\frac{1}{2}$	1	2.76	2.68	1.85
$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	3.08	2.44	2.31
$\frac{1}{4}$	$\frac{3}{4}$	1	3.13	2.67	2.38
$\frac{1}{4}$	1	1	3.20	2.66	2.66
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3.10	1.90	1.90
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}$	3.41	2.38	1.95
$\frac{1}{2}$	$\frac{1}{2}$	1	3.44	2.67	1.97
$\frac{1}{2}$	$\frac{3}{4}$	$\frac{3}{4}$	3.79	2.45	2.29
$\frac{1}{2}$	$\frac{3}{4}$	1	3.85	2.67	2.36
$\frac{1}{2}$	1	1	3.90	2.66	2.66
$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	4.27	2.46	2.46
$\frac{3}{4}$	$\frac{3}{4}$	1	4.38	2.66	2.47
$\frac{3}{4}$	1	1	4.50	2.66	2.66
1	1	1	4.72	2.67	2.67

$\varphi_1\varphi_2\varphi_3\omega$ space. At points where two frequencies are equal the frequency branches change from one smooth surface to the other. The branch of highest frequency contains mainly longitudinal, the two other mainly transverse vibrations.

This combination of vibrations enables one to interpolate frequency values at other points of the phase cube. The frequencies have been interpolated at points in the center between each pair of points of distance $\frac{1}{4}\pi$. To find, following Blackman, the number of vibrations in frequency intervals the whole frequency range has been divided into 24 intervals and three sets of curves of constant frequency, corresponding to the three frequency branches, have been determined in the 9 planes $\varphi_3 = 0, \frac{1}{8}\pi, \frac{1}{4}\pi, \cdots \pi$. By means of graphical integration the areas between curves of constant frequency have been evaluated and from these the volumes between surfaces of constant frequency for all three branches have been determined by repeated graphical integration. These volumes are proportional to the number of characteristic vibrations. The smooth curve in each frequency interval containing the number of vibrations which has been calculated in this way was assumed to be the distribution function.

The two branches of lower frequency show maxima of vibration density near the residual ray frequency. The lowest branch has this frequency as maximum frequency, the medium branch has a small number of vibrations with frequencies higher than the residual ray frequency. Both have second density maxima at lower frequencies, thus causing a second maximum of the distribution of all three branches together. The branch of highest frequency has its maximum also near the residual ray frequency but has a high number of vibrations between this

and almost the double frequency. Figure 1 gives the sum of the distribution functions of all three branches.

Specific Heat

The specific heat of a system of N oscillators of frequency ν is given by

$$C_v = kN \int^{\nu_{max}} \frac{(h\nu/kT)^2 \exp(h\nu/kT)}{(\exp[h\nu/kT]-1)^2} \frac{dn}{d\nu} d\nu.$$

In the case of a quadratic distribution function $dn/d\nu = \text{const.} \times \nu^2$, with a maximum frequency, which is determined by the total number of degrees of freedom, a characteristic temperature θ can be defined, which is related to the maximum frequency by $\theta = h\nu_{max}/k$.

For the lower frequencies the distribution function of the KCl crystal is in agreement with the Debye quadratic distribution of the continuum with the characteristic temperature $\theta = 230°$. This θ value is in agreement with the value obtained from specific heat measurements because this parabola is a good approximation for the distribution function even at higher frequencies because it continues to frequencies higher than the residual ray frequency. However, in temperature intervals where the first maximum of the distribution function gives the main contribution one may expect a minimum of the corresponding θ values of the continuum which would give the same specific heat at this temperature. Blackman's qualitative considerations

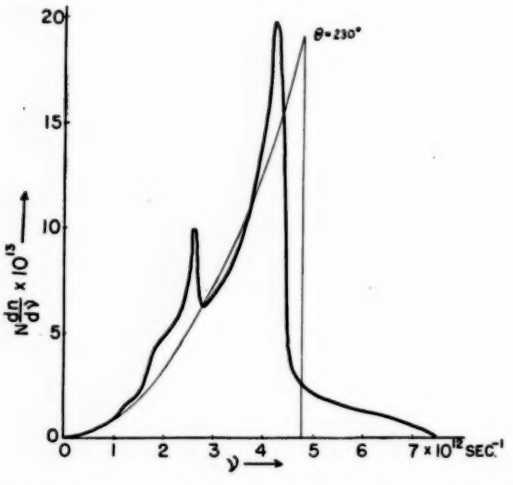

Fig. 1. Density distribution of the lattice vibrations of the KCl crystal.

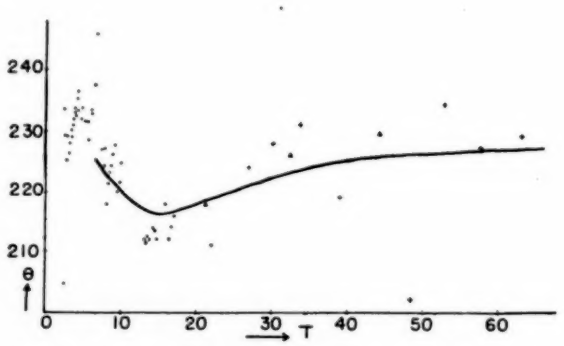

Fig. 2. Specific heat. ●—Keesom and Clark. +—Nernst and Lindemann. ▲—Southard and Nelson. ——calculated.

and Kellermann's[12] calculation of the NaCl crystal show the same feature. It is hardly possible to give a quantitative discussion of this feature without calculating the distribution with elastic constants at lower temperatures. But under the assumption that the distribution function does not change with temperature, although the elastic constants do,[13] the dependence of the characteristic temperature on the absolute temperature can be calculated. This leads to the function given in Fig. 2. In this diagram the experimental values given by different authors are also plotted. Keesom and Clark[14] find a probable increase of θ in a range between 2°K and 4°K but it is not possible to make any decision about the reality of such an increase from the present calculations because the frequency intervals used are too large and the number of calculated frequencies too small. Above these temperatures they find a decrease to about 17°K, but the given values may be interpreted as a slight increase for θ at the end of this interval. The measurements are extended to higher temperatures by Nernst and Lindemann,[15] and Southard and Nelson.[16] The combined values seem to indicate a minimum near 15°K.

I am much indebted to Professor I. Waller for suggesting this subject and for much advice during the work and to Internationella Studenthjälpen (I.S.S.) Uppsala for making it possible for me to do this work.

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Range-Velocity Relation for Fission Fragments in Helium

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The range-velocity relation of fission fragment tracks in helium has been studied by means of individual close collisions as well as by statistical considerations of the branch frequency. The comparison with previous investigations of fragment tracks in argon indicates that the shape of the range-velocity curves for the two gases differs appreciably in the last part of the range just as was to be expected from theoretical considerations concerning the relative contributions to the stopping power by electron encounters and nuclear collisions in light and heavy gases.

AS reported in previous papers,[1] cloud-chamber tracks of fission fragments in argon as well as in helium have been obtained in this Institute. While the tracks in argon offered sufficient material for a detailed study of the range-velocity relation, the tracks in helium were so far mainly used for range measurements. The ratio between the range of the fission fragments and the range of α-rays was in helium found to be about 20 percent larger than the corresponding ratio in argon. As pointed out by Professor Bohr, this difference is just in agreement with the different shape of the range-velocity curves in light and in heavy gases to be expected from theoretical considerations.[2]

In fact, the range-velocity curve consists of an almost linear slope extending over the larger part of the range, and an end part, where the rate of velocity loss to begin with decreases and, after passing through a minimum, rapidly increases corresponding to a steep descent of the curve at the very end of the range. The stopping in the first part is due almost entirely to electronic encounters, whereas the stopping in the later part is mainly caused by nuclear collisions, the effect of which becomes preponderant when the total charge of the fragment is nearly neutralized by electron capture. While the electronic stopping effect in different gases is proportional to the stopping power for α-rays of the same velocity, the nuclear stopping effect increases far more rapidly with the atomic number of the gas. This means that the end part of the range should be relatively longer in a light gas than in a heavy one, and in helium it was estimated to be three times as long as in argon. Since in this gas the end part is roughly 10 percent of the range, it should be about 30 percent in helium, and the whole range in helium relative to α-rays ought therefore to be just about 20 percent longer than in argon.

In view of the theoretical interest of a closer examination of this question the experiments were continued, and a large number of cloud-chamber pictures of fission fragment tracks in helium have recently been obtained which allow a direct investigation of the range-velocity curve in this gas. A few typical examples of such pictures are given in Fig. 1 where, for comparison, one of the older photographs in argon is also shown. As seen, the tracks in helium are less curved than in argon, as was to be expected from theory,[3] since the mean deviation over a part of the range with a given velocity loss should be proportional to the square root of the atomic number; furthermore, the number of branches of a given length is considerably greater in helium due to the larger range of recoil particles of the same energy in helium than in argon.

The previous papers contain a discussion of two different ways of velocity determination, *viz.*, the usual direct method by means of individual close collisions, and a statistical method based on an examination of the branch frequency along the range. The first method has the advantage of giving absolute values but the reliability of the velocity determination depends upon the certainty of the identification of the particles

[1] K. J. Brostrøm, J. K. Bøggild, and T. Lauritsen, Phys. Rev. **58**, 651 (1940); N. Bohr, J. K. Bøggild, K. J. Brostrøm, and T. Lauritsen, Phys. Rev. **58**, 839 (1940); J. K. Bøggild, K. J. Brostrøm, and T. Lauritsen, Phys. Rev. **59**, 275 (1941); J. K. Bøggild, K. J. Brostrøm, and T. Lauritsen, D. Kgl. Danske Vid. Selsk. Math.-fys. Medd. (Math.-phys. Comm., Acad. Sci. Copenhagen) **18**, (1940).

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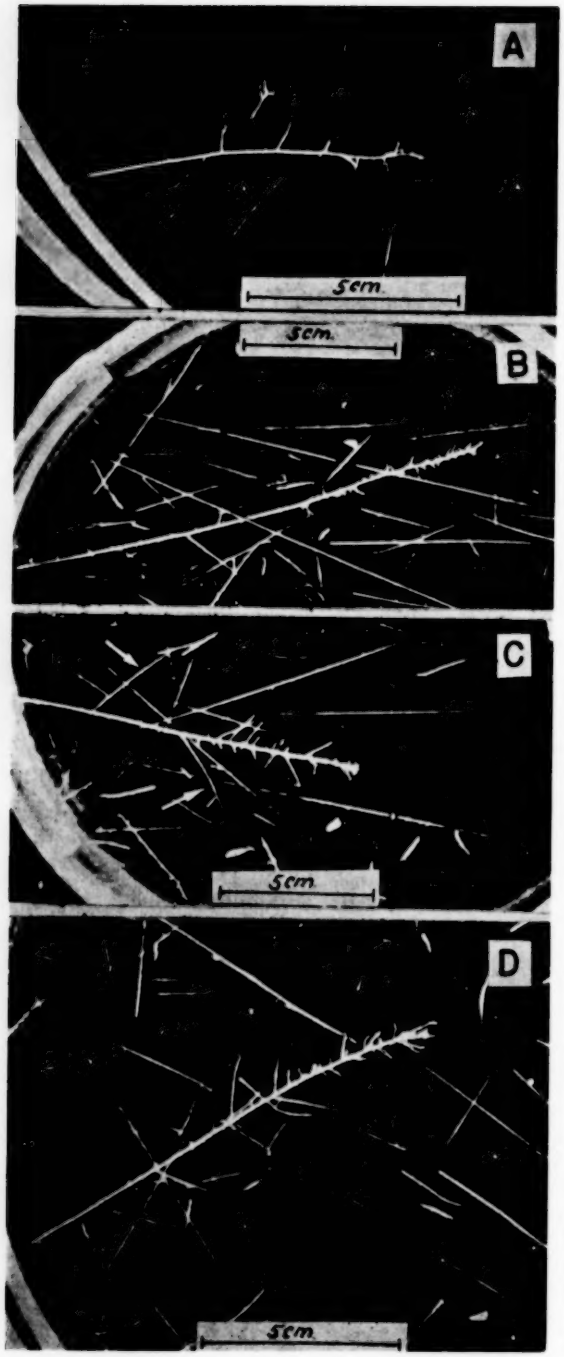

FIG. 1. A. Track in argon showing fortuitous bending and several branches all more intense than the protons and α-ray tracks appearing as background. Fine parallel lines are wires fastened to the underside of the glass cover to provide conducting surface for sweep field. ($A+H_2O+C_2H_6O$, total pressure 10 cm). B. Track in helium showing a close collision with a helium nucleus rather early in the range and numerous collisions on the last part. C. Track with several long helium branches suitable for velocity determination especially the two indicated by arrows. D. Track in helium with at least 30 collisions giving branches of more than 2-mm range. The forked track in the center of the picture is not a branch but a helium recoil nucleus produced by neutron impact and colliding after a path of few mm in the chamber with another helium nucleus. ($B-D$: $He+H_2O$, total pressure 34 cm.)

involved in the collision and of the knowledge of the range-velocity relation for these particles. The branch statistics gives information about the range-velocity relation by simply counting in various sections of the range the number of branches with lengths within given limits. This number is, in fact, inversely proportional to the square of the average velocity of the fragment in the respective range section. This method has the advantage that it is independent of other information, but the velocity determinations are only relative.

In the investigation of the range-velocity relation in argon the statistical method was mainly used, since the mean error of the direct velocity determination even under the most favorable conditions was about 20–30 percent. In helium, however, the direct velocity determination is practicable with greater exactness due to the fact that the collisions with helium nuclei are rather easy to distinguish from collisions with heavier and lighter atoms present in the cloud chamber. In the present investigation, both methods of velocity determination could therefore be used and gave results supporting each other. The experimental arrangement was the same as that described in the previous papers with the only difference that the water-alcohol mixtures used at that time were now replaced by pure water in order to reduce the stopping power of the vapor in the cloud chamber. The uranium was placed as a "thick" layer on a copper strip near the wall of the chamber.

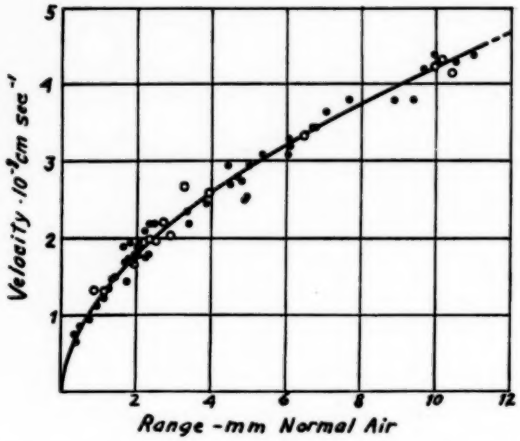

FIG. 2. Range-velocity curve in helium derived from individual close collisions with helium nuclei (full circles) and with heavier nuclei (open circles).

The determination of the velocity of the fragments is given by the formula

$$v = u\left[\frac{(1+k)^2}{4\cos^2\theta} - k\right]^{\frac{1}{2}},$$

where k is the ratio of the masses of the gas nucleus and the fission fragment, u and v are the velocities of these particles after the collision, and θ is the angle between the direction of the stem of the track before the collision and the direction of the branch. In collisions with helium nuclei the velocity u was yielded by means of the energy-range relation for α-particles,[4] the range of the helium branches being converted into normal air values by use of the stopping power coefficient of the gas. This stopping power was measured directly by means of a beam of α-rays with a residual range of 12.5-mm normal air, admitted through a window in the side of the chamber. Since the stopping power of the gas turned out to be somewhat larger than it would corresponding to pure helium and water vapor, the helium gas was examined spectroscopically and was found to contain some nitrogen. Therefore, in the collisions with heavier nuclei, the mass was estimated to be 15, and the velocity u was determined by a curve halfway between the range-velocity curves for oxygen and nitrogen of Blackett and Lees[5] with the values of the velocity increased by 5 percent.[6]

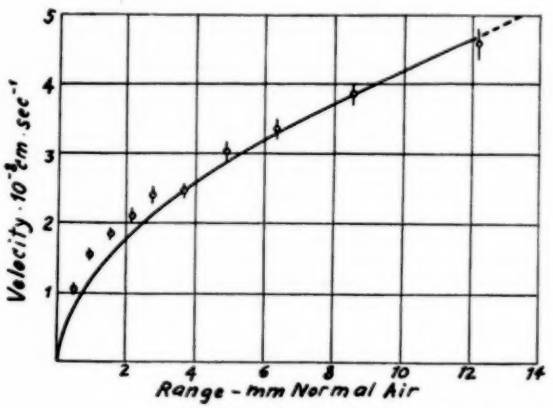

FIG. 3. Range-velocity relation in helium derived from statistic of branch distribution.

[4] Cornell University curves (1938).
[5] P. M. S. Blackett and D. S. Lees, Proc. Roy. Soc. **A134**, 660 (1931).
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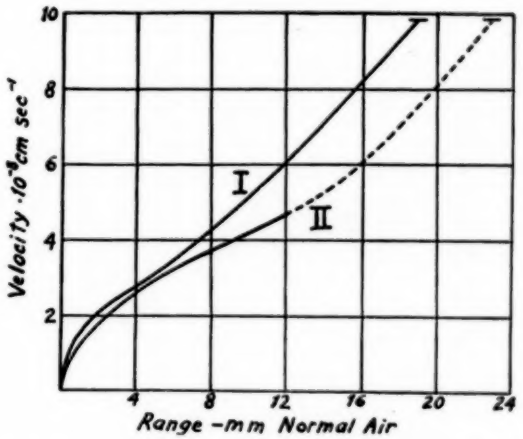

FIG. 4. Range-velocity relation in argon (curve I) and in helium (curve II).

The present investigation includes 34 fragment tracks at about 25-cm gas pressure and 83 fragment tracks at about 34-cm pressure. Among these, 49 collisions with helium nuclei and 15 with heavier nuclei are suitable for velocity determination; the results of these measurements are reproduced in Fig. 2, where the velocity is given in relation to the residual fragment range converted into normal air. The small full circles refer to the collisions with helium nuclei and the open circles refer to the collisions with heavier nuclei, and it will be seen that the two kinds of collisions within the experimental errors give consistent velocity determinations. The curve drawn on Fig. 2 to fit all the points as closely as possible must be taken as an average curve for the range-velocity relations for the lighter and heavier groups of fission fragments, and the relatively small spread of the points shows that the velocity curves of the two fragments differ only little within the last 10 mm of the range.

The experimental material was also subjected to a statistical examination on the basis of 83 tracks at 34-cm gas pressure, including in all about 1100 branches of length between 2.3 and 10 mm, i.e., 0.26–1.14 mm normal air. The relative velocities thus calculated are reproduced in Fig. 3 in such a scale that for the larger velocities agreement is obtained with the range-velocity curve derived from the direct velocity determinations which is here reproduced from Fig. 2. The circles with the vertical lines represent mean values and probable errors of the relative velocities. Although the points fall

rather close to the curve, the deviations for the smaller velocities are larger than the estimated experimental errors indicating some minor defects in the one or the other of the two methods of velocity determination. In the statistical method such a defect might perhaps be due to a failure to count all branches in the last, more branching part of the range; in the direct method a defect might be due to a possible inaccuracy in the assumed range-velocity relation of the α-particles in helium for the smallest velocities.

A comparison of the range-velocity relation in argon and in helium is attempted in Fig. 4. Here, curve I is an average range-velocity curve for the two groups of fission fragments in argon obtained in the previous paper. In curve II, the full-drawn part corresponds to the information contained in Fig. 2, while the dotted part is drawn in a way that the total average range is 4-mm normal air greater than in argon, in accordance with the earlier measurements. Although the information on which the upper parts of curves I and II are based is rather scanty, it seems that there can be no doubt about the general run of the curves. In particular, the point where the rate of velocity loss is a minimum is obviously much farther removed from the end of the range in helium than in argon. The shape of the curves seems altogether to fit the theoretical expectations, and the curves can, at least within the experimental errors, be drawn in such a way that the rate of velocity loss is alike in the two gases in the first part of the range where the stopping is mainly due to electron encounters, whereas the end part of the range-velocity curve in helium is considerably longer than in argon, corresponding to the effect of the smaller energy loss by nuclear collisions in helium than in argon.

The author wishes to express his heartiest thanks to Professor Niels Bohr for his constant interest in this work and for many helpful discussions. I am also much obliged to Dr. E. Rasmussen for the spectroscopical analysis of the helium and to Mr. K. Lindberg-Nielsen and Mr. H. Arrøe whose assistance in the experiments has been of great value.

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On the Pseudoscalar Mesotron Theory of β-Decay

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The calculations of Sakata which indicate that the pseudoscalar mesotron theory can successfully account for both mesotron decay and β-decay are shown to be in error. While the pseudoscalar mesotron theory gives the correct spin and parity selection rules for β-decay, it also gives β-decay lifetimes too long by a factor of 10^6 and having an inverse seventh power dependence on the upper limit of the β-spectrum. As these same conclusions can be made when the mesotron field is strongly coupled to nuclear particles, it would seem that they are sufficient to show that pseudoscalar mesotrons are not responsible for β-decay.

YUKAWA'S[1] suggestion that β-decay is to be interpreted as the emission of a mesotron by a neutron (or proton) and its subsequent decay into an electron (or positron) and a neutrino has received support from the observed instability[2] and apparent β-radioactivity of cosmic-ray mesotrons. However, before it can be regarded as a correct description of nuclear β-processes, it must give rise to a theory of β-decay possessing the following features: (1) Fermi energy distribution[3] with its consequent inverse fifth power dependence of the lifetime on the upper limit of the spectrum,[4] (2) Gamow-Teller selection rules,[4,5]

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[3] J. L. Lawson, Phys. Rev. **57**, 982 (1940).
[4] M. G. White, E. C. Creutz, L. A. Delsasso, and R. R. Wilson, Phys. Rev. **59**, 63 (1941).
[5] T. Bjerge and K. J. Brostrøm, Kgl. Danske Vid. Sels. Math.-fys. Medd. **16**, No. 8 (1938).

(3) calculated lifetimes of β-radioactive nuclei, with the mesotron-electron-neutrino coupling constant evaluated from the disintegration of the free mesotron and the mesotron-nuclear particle coupling constant evaluated from nuclear forces, in agreement with experiment. The scalar mesotron theory meets only the first point; the vector theory but the first two. Both these theories give β-decay that is too slow.[6-8] Its characteristic time, that factor in the lifetime independent of the energy and matrix element of the transition, is of the order of a hundred times greater than that evaluated from experiments on light nuclei.

Christy and Kusaka's[9] analysis of cosmic-ray bursts together with the spin dependence of nuclear forces indicates that mesotrons are best described by a pseudoscalar field.[10,11] Recently, the assertion has been made that pseudoscalar mesotrons provide a theory of β-decay in agreement with experiment. Calculations by Sakata[8] yielded the necessary "allowed" β-decay and slow disintegration of the free mesotron. However, his formula for β-decay turns out to be incorrect;[12] proper treatment of the problem shows that the lifetime discrepancy remains and is, in fact, increased from a factor of 10^2 to a factor of 10^6.

Yukawa treats the connection between nuclear forces and β-decay with an interaction of the mesotron field with nuclear particles and with electrons and neutrinos symmetrical in all respects except in strength. In the pseudoscalar theory this is expressed in the following Lorentz-invariant terms in the Lagrangian:

$$L=-(8\pi)^{\frac{1}{2}}\int dV_4\Big\{\frac{2M}{\mu}g\psi^\dagger\gamma^5\frac{(\tau_x+i\tau_y)}{2}\psi U+\frac{2M}{\mu}g\psi^\dagger\gamma^5\frac{(\tau_x-i\tau_y)}{2}\psi U^*+g'\varphi^\dagger\gamma^5\frac{(\tau_x+i\tau_y)}{2}\varphi U+g'\varphi^\dagger\gamma^5\frac{(\tau_x-i\tau_y)}{2}\varphi U^*\Big\}. \quad (1)$$

U is the pseudoscalar field and U^* its complex conjugate. ψ and φ are the neutron-proton and the electron-neutrino wave fields, $\psi^\dagger=i\psi^*\beta$ and $\varphi\dagger=i\varphi^*\beta$ their respective adjoints. γ^5 and β are Dirac matrices, τx and τy are isotopic spin matrices, $M=$ proton mass, and $\mu=$ the mesotron mass. The mesotron-nuclear particle coupling constant g is normalized so that the potential in the singlet state of the deuteron is $g(e^{-\kappa r}/r)$, $\kappa=\mu c/\hbar$.

It might be expected that interaction terms containing the first derivatives of U as well as ones containing U should occur in the Lagrangian. However, such terms do not really represent a different type of interaction, for in virtue of the equations of motion of ψ, they may be derived from the terms in (1) by partial integration.

$$\psi^\dagger\gamma^5\frac{(\tau_x+i\tau_y)}{2}\psi\cong-\frac{\hbar\partial_\nu}{2Mc}\Big\{\psi^\dagger\gamma^5\gamma^\nu\frac{(\tau_x+i\tau_y)}{2}\psi\Big\}.$$

The neglected terms are of the order g^2, are bilinear in the U fields, and give no contribution to β-decay. They also give no contribution to nuclear forces in the usual approximations. Thus there is no need to introduce two independent constants, f and g, in the pseudoscalar theory as there is in the vector theory.

Since (1) does not contain the time derivative of U, i.e., the canonically conjugate field momentum, the interaction terms in the Hamiltonian are just the negative of the ones in L.

$$H_{\text{int}}=-L. \quad (2)$$

In this formulation there are no terms directly coupling neutrons and protons to electrons and neutrinos in either the Hamiltonian or the Lagrangian. Such terms do appear in the

[6] H. Yukawa, S. Sakata, M. Kobayasi, and M. Taketani, Proc. Phys. Math. Soc. Japan **20**, 720 (1938).
[7] H. A. Bethe and L. W. Nordheim, Phys. Rev. **57**, 998 (1940).
[8] S. Sakata, Proc. Phys. Math. Soc. Japan **23**, 291 (1941).
[9] R. F. Christy and S. Kusaka, Phys. Rev. **59**, 405, 414 (1941).
[10] J. R. Oppenheimer, Phys. Rev. **59**, 462 (1941).
[11] J. R. Oppenheimer and J. S. Schwinger, Phys. Rev. **60**, 150 (1941).
[12] Sakata has apparently neglected the singularity arising from the derivatives of the Yukawa potential in his Eq. (79d). As has been pointed out by Serber, reference 7, $\boldsymbol{\sigma}_1\cdot\boldsymbol{\nabla}_1\boldsymbol{\sigma}_2\cdot\boldsymbol{\nabla}_2$ (exp $(-\kappa|\mathbf{r}_1-\mathbf{r}_2|)/|\mathbf{r}_1-\mathbf{r}_2|$), which also occurs in the Bethe-Nordheim, reference 7, treatment of the vector theory, contains $(4\pi/3)\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2\delta(\mathbf{r}_1-\mathbf{r}_2)$. Upon integration over the electron-neutrino coordinates in the matrix element for β-decay, this delta function term cancels in the usual approximation for "allowed" transitions, wave functions of electron and neutrino treated as constant over nuclear dimensions, the $-(4\pi/3)\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2$ from the other terms.

Hamiltonian in the equivalent formulation in which derivatives of U occur in the interaction Lagrangian. There the inclusion of such terms in the Hamiltonian is essential to preserve the covariance of the theory and to give the same matrix elements as (2). Any attempt to eliminate them by adding invariant direct interaction terms to the Lagrangian succeeds only in replacing them by larger ones.

The matrix element, H_{if}, for β-decay follows from (2) by a straightforward calculation using second-order perturbation theory, and plane Dirac waves for the electron and neutrino.

$$H_{if}=\frac{gg'(\hbar c)^2}{W^2-E_k^2}BB', \tag{3}$$

$$B=\frac{2Mi}{\mu}\sum_s\int dV\Psi_f^*\beta_s\gamma_s^5\frac{(\tau_x^s+i\tau_y^s)}{2}\times\Psi_i\exp[-i\mathbf{k}\cdot\mathbf{r}_s], \tag{3'}$$

$$B'=iu_e^*\beta\gamma^5u_\nu.$$

Ψ_i and Ψ_f are the initial and final wave functions of the nucleus. The summation s is carried out over all the particles in the nucleus. u_e and u_ν are the spin functions of the electron and the neutrino.

W = upper limit of the β-spectrum,
E_k = energy of the mesotron,
$\hbar\mathbf{k}$ = its momentum.

Since by the equations of motion of ψ in non-relativistic approximation

$$\psi^\dagger\gamma^5\frac{(\tau_x+i\tau_y)}{2}\psi\cong\frac{\hbar}{2iMc}\nabla\cdot\left(\psi^*\boldsymbol{\sigma}\frac{(\tau_x+i\tau_y)}{2}\psi\right), \tag{4}$$

$$B=\frac{\hbar\mathbf{k}}{c\mu}\cdot\sum_s\int dV\Psi_f^*\boldsymbol{\sigma}_s\frac{(\tau_x^s+i\tau_y^s)}{2}\times\Psi_i\exp[-i\mathbf{k}\cdot\mathbf{r}_s]=\frac{\hbar\mathbf{k}}{c\mu}\cdot\mathbf{B}_1 \tag{4'}$$

$\boldsymbol{\sigma}$ represents the Pauli spin matrices. The transition probability for β-decay is:

$$\frac{1}{\tau}=\frac{2\pi}{\hbar}\int d\Omega_e\int d\Omega_\nu\int_{mc^2}^{W}dE_e|H_{if}|^2\rho_e\rho_\nu,$$

$$\rho_e=\frac{P_e^2dP_e}{(2\pi\hbar)^3dW},\quad \rho_\nu=\frac{P_\nu^2}{(2\pi\hbar)^3}\frac{dP_\nu}{dW}.$$

E_e = energy of the electron,
$\mathbf{P}_e$ = momentum of the electron,
E_ν = energy of the neutrino,
$\mathbf{P}_\nu$ = momentum of the neutrino,

$$\mathbf{P}_e+\mathbf{P}_\nu=\hbar\mathbf{k},$$

$$\sum_{\text{spins of }e\text{ and }\nu}|B'|^2=1-\frac{\mathbf{P}_e\cdot\mathbf{P}_\nu c^2}{E_eE_\nu}, \tag{5}$$

$$\frac{1}{\tau}=\frac{1}{\tau_\beta}\frac{1}{3}|\mathbf{B}_1|^2I(\omega_0), \tag{6}$$

$$\frac{1}{\tau_\beta}=\frac{32}{\pi}\frac{\mu c^2}{\hbar}\left(\frac{gg'}{\hbar c}\right)^2\left(\frac{m}{\mu}\right)^7, \tag{7}$$

m = mass of the electron,

$$I(\omega_0)=\int_1^{\omega_0}d\omega\left\{\frac{8\omega(\omega-\omega_0)}{3}+\omega_0^2+\frac{2\omega_0}{\omega}-\frac{5}{3}\right\}\times\omega(\omega^2-1)^{\frac{1}{2}}(\omega_0-\omega)^2$$

$$=(\omega_0^2-1)^{\frac{1}{2}}\left\{\frac{\omega_0^6}{70}-\frac{13\omega_0^4}{140}-\frac{4\omega_0^2}{21}+\frac{2}{105}\right\}+\frac{\omega_0^3}{4}\ln[\omega_0+(\omega_0^2-1)^{\frac{1}{2}}]\sim\omega_0^7/70, \tag{8}$$

$$\omega=Ee/mc^2,\quad \omega_0=W/mc^2.$$

It is instructive to compare B, the nuclear matrix element, and B', the electron-neutrino matrix element, (3) in the special case of the decay of the neutron. Here all the particles may be appropriately described by using plane waves. The contribution of B' is expressed in (5). Since both the neutron and proton have non-vanishing rest mass, the contribution of B differs from that of B' by mass terms.

$$\sum_{\text{spins of }P\text{ and }N}|B|^2=\left(\frac{2M}{\mu}\right)^2\left(1-\frac{\mathbf{P}_N\cdot\mathbf{P}_Pc^2+M_NM_Pc^4}{E_NE_P}\right)=\left(\frac{2M}{\mu}\right)^2\frac{(\mathbf{P}_P)^2c^2}{2(M_Pc^2)^2}=\left(\frac{2M}{\mu}\right)^2\frac{(\mathbf{P}_e+\mathbf{P}_\nu)^2}{2(M_Pc)^2}\sim\left(\frac{m}{\mu}\right)^2, \tag{5'}$$

while (5) is of the order unity.

The presence of $\boldsymbol{\sigma}$ in B (4') ensures Gamow-Teller selection rules. Although $\beta\gamma^5$ is a pseudo-

scalar, there is no parity change in the nuclear state in the most "allowed" transition. This is so because B vanishes in view of (4) when $\exp[-i\mathbf{k}\cdot\mathbf{r}]$ is replaced by the first term, 1, in its expansion and the most "allowed" transition comes from the second term in the expansion, $-i\mathbf{k}\cdot\mathbf{r}$, which when multiplied by $\beta\gamma^5$ does not change sign under reflection of the space coordinates. Since B is proportional to the momentum of the mesotron, the lifetime τ has an inverse seventh power dependence on the upper limit of the β-spectrum in disagreement with the inverse fifth power dependence shown by the series of light positron emitters.[4]

Only slow mesotrons are involved in β-decay, $\hbar k \ll \mu c$. Thus the $\hbar\mathbf{k}/\mu c$ in B contributes, upon averaging over the angles of the electron and neutrino, effectively $(m/\mu)^2$ to the transition probability, slowing up β-decay in that proportion.

The probability per unit time that a free pseudoscalar mesotron decay, obtained after a similar but simpler calculation, is

$$1/\tau_\mu = (\mu c^2/\hbar)(g'^2/\hbar c) \tag{9}$$

from (7) and (9)

$$\tau_\beta = \tau_\mu \frac{\pi}{32}\frac{\hbar c}{g^2}\left(\frac{\mu}{m}\right)^7$$

with $\tau_\mu = 2\times 10^{-6}$ sec., $g^2/\hbar c = 0.1$, $\mu = 200$ m, $\tau_\beta{}^{\text{calc}} = 2.4(10)^{10}$ sec. while from (6) and experiments on Ne^{19},[4] $\tau_\beta{}^{\text{exp}} = 6.7(10)^3$ sec. $\tau_\beta{}^{\text{calc}}/\tau_\beta{}^{\text{exp}} \sim 10^6$, a discrepancy greater by $(\mu/m)^2$ than that in the scalar or in the vector theory.

In deriving these results perturbation-theoretic methods have been used. The large mesotron-nuclear particle coupling renders these methods unsuited to many problems. However, recent investigation of this interaction in the limit of strong coupling, with extended sources used to ensure convergence, indicates that the normal state of the field of pseudoscalar mesotrons "bound" to nuclear particles differs from the classical static field only by a factor of $1/\sqrt{6}$.[13] Since the classical field gives for β-decay the same results as perturbation theory, no new feature, except the $\frac{1}{6}$ which only increases the lifetime discrepancy, is introduced into this problem by strong coupling. For allowed transitions β-decay does not depend on the details of the source. As preliminary results of strong coupling calculations indicate that $g^2/\hbar c$ is not a large number,[11] it is unlikely that a detailed treatment of the problem would produce results altered enough to give a correct description of β-decay. Therefore, it would seem that the magnitude of the lifetime discrepancy and the seventh power energy dependence are sufficient to show that pseudoscalar mesotrons are not responsible for β-decay.

Two alternative interpretations of β-decay have been suggested: (1) There are two kinds of mesotrons—long-lived pseudoscalar mesotrons observed near sea level in cosmic rays and fast decaying mesotrons of another type to give β-decay.[14] Møller and Rosenfeld[15] suggested, for other reasons, a theory giving a combination of pseudoscalar and vector mesotron fields in nuclei. Rozental has shown that the constants in this theory can be chosen to give correctly the observed mesotron decay and β-decay.[16] (2) β-decay occurs as in the original Fermi theory by means of a direct interaction between the nuclear particles and electrons and neutrinos. Since the constant characterizing this interaction is dimensionally different from that which couples mesotrons to electrons and neutrinos, it does not seem possible to relate them in any unique way and establish thereby a simple connection between β-decay and the decay of a free mesotron. The suggestion[17] that mesotron decay occurs through the virtual emission of a neutron-proton pair is dependent on a highly speculative application of a not yet substanstiated relativistic theory of neutrons and protons.

The author wishes to thank Professor J. R. Oppenheimer for suggesting this problem and for his continued interest in this work and Dr. J. S. Schwinger and Dr. E. P. Cooper for their helpful discussions.

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Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the eighteenth of the preceding month, for the second issue, the third of the month. Because of the late closing dates for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Communications should not in general exceed 600 words in length.

Slowing Down of Low Energy Neutrons in Water

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October 15, 1941

THE slowing down in water of the fast neutrons emitted by a Rn-α-Be source has been studied extensively by many investigators, particularly by Amaldi and Fermi.[1] Figure 1a, taken from their work, shows how the intensity inside water of neutrons of thermal energy (C neutrons) and neutrons of an energy of a few ev (D, A+B, I, in order of increasing energies) varies with the distance from the source. The striking feature, that at large distances from the source the curves for C and resonance neutrons are rather similar, was explained qualitatively as due to the fact that the average mean free path for scattering of the fast primary neutrons which have energies up to 12 Mev is of the order of 5 cm, whereas that of the resonance neutrons is less than 1 cm, and the diffusion length of the C neutrons is 2.1 cm. At some distance from the source, equilibrium conditions are approached: The character of the curves is now governed in the main by the largest of these three values, i.e., the mean free path of the primary neutrons, and hence the intensities of resonance and C neutrons decrease in a similar manner. This implies that the intensity of the resonance neutrons does at no point in the water become negligible compared with that of the C neutrons. This important result has often been considered as quite generally true, independent of the neutron source used.

However, a different situation might be expected when the neutron source emits neutrons of low, and preferably homogeneous, energy. For neutrons of a few hundred kev energy, the mean free path for scattering in water is about 1 cm, only a little larger than for resonance neutrons, but well below the diffusion length of C neutrons. For such primary neutrons, one might therefore expect to find much less similarity between the Amaldi-Fermi curves for resonance and C neutrons. This is borne out by the following experiment.

As a neutron source we used the photo-neutrons produced in beryllium by the hard γ-rays of radio-yttrium (100d). The RdY, of an initial intensity of about 30 millicuries Ra equivalent, was produced in the 60-inch Berkeley cyclotron by the reaction $Sr(d, 2n)Y$.[2] The RdY+Be neutrons have an energy of 220±20 kev, as determined from the energy of the recoil protons by Scharff-Goldhaber.[3] The C and D neutrons were measured with an indium foil detector (54 min.) and the I neutrons with an iodine detector (PbI_2). The results are shown in Fig. 1b. It is seen that at a large distance from the neutron source, the intensity of the resonance neutrons decreases much faster than that of the C neutrons. In this way one can obtain C neutrons practically free from resonance neutrons.

We have observed similar effects with other photo-neutron sources. A detailed report of this work will appear in due course.

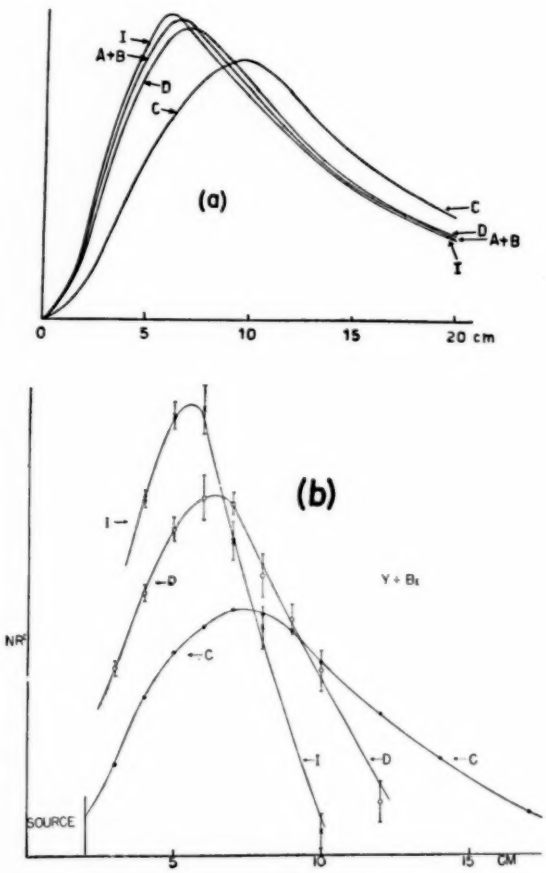

FIG. 1. Ordinates = activation $\times r^2$. Abscissae = r = distance of detector from center of source. The units of the ordinates are chosen so that each curve includes the same area. (a) Taken from Amaldi and Fermi, reference 1, p. 918, Fig. 7. Rn-α-Be neutrons; (b) RdY+Be neutrons.

The radio-yttrium source was produced in Berkeley by the late Dr. C. Pecher. We wish to thank Professor E. O. Lawrence for generously permitting us to use this valuable source indefinitely.

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The Change in the Electric Resistance of a Single Crystal of Magnetite by Magnetic Field at Low Temperatures

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THE change in electric resistance of a single crystal of magnetite at low temperatures, 0° (ice water), −95° (freezing point of toluol) and −195° (liquid nitrogen) was measured up to 1200 oersteds in longitudinal magnetic field, and the intensity of magnetization of the specimen was also measured under the same condition. The specimen is a rectangular crystal rod, 3.43 mm² in sectional area and 6.0 mm in length, which was cut off from a block of perfect natural crystal from Kamaishi, Japan; the axis of the rod coincides with the direction of a principal axis [111]. Each end of the specimen was soldered to a copper lead wire by aid of platinum chloride melted in lavender oil. The resistance was measured with a potentiometer. The amount of current through the specimen at 0°, −95°, and −195° was 0.02, 0.01, and 0.001 ampere, respectively. The intensity of magnetization was measured by means of the ballistic method; the demagnetizing factor used was that given by R. Mann.

The results of measurement are shown in Fig. 1, in which the lower half is the relation between the change of $\Delta R/R$ and the longitudinal magnetic field H, the magneto-resistance curve, and the upper half is the relation between the intensity of magnetization I and H, the magnetization curve. From this figure, we see that the change of resistance is negative for all field strengths at temperatures below zero. This negative magneto-resistance effect has been observed only in Fe-Si alloys,[1] but not in the alloys of Ni-Cu,[2] Ni-Co, Fe-Ni and Fe-Co.[3] The change of resistance at 0° and −95° decreases at first rapidly and then slowly with the increase of the field, while at −195°, it decreases linearly. The different form in these curves is to be attributed to the difference of the states before and after the allotropic transformation of magnetite in −158°∼−166°.[4] By the same cause, the magnetization curves at 0° and −95° are different in form from that at −195°. In the transversal field the change of resistance shows the same behavior as shown in the ferromagnetic metals.

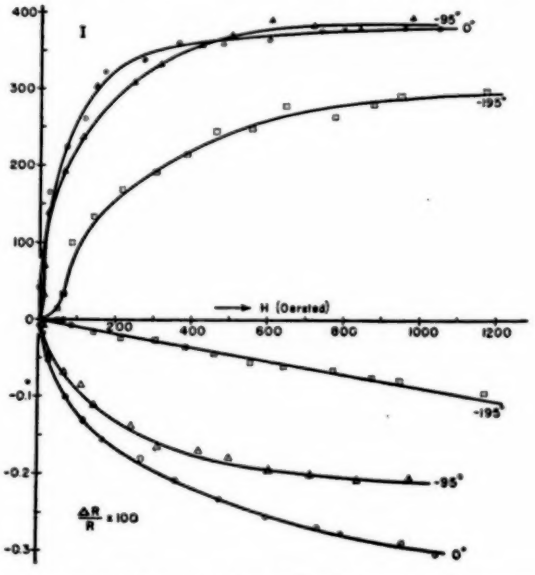

FIG. 1. Magneto-resistance and magnetization curves at low temperatures for magnetite having principal axis [111].

The decrease of resistance in the ferromagnetic compound is very interesting and will be studied in the other principal axes of magnetite in the near future.

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Meson Theory and Nuclear Forces

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October 9, 1941

AS is well known, the nuclear interaction predicted by meson theory contains terms so strongly singular ($\sim -1/r^3$) that some kind of cutting off procedure must be adopted when applying it as potential energy in the Schrödinger equation.

However, there is a second possibility discussed by Bethe,[1] but finally discarded by him, namely, that the diverging terms may have a significance analogous to the magnetic interaction between electrons. In that case the situation would be entirely different, because, as Breit has shown,[2] such terms cannot simply be considered as part of an energy operator in configuration space.

In fact, there are reasons for believing that the meson interaction and Breit's operator have a similar origin. To demonstrate this, we modify the derivation of nuclear forces from field theory in the following way:

If the homogeneous equations governing the meson field in vacuum are

$$\frac{\partial^2\phi_i}{\partial x_\mu \partial x^\mu} - \kappa^2\phi_i = 0,$$

one may ask what are the inhomogeneous equations for the field generated by the heavy particles.

Clearly the right-hand side must be a four vector. Now the simplest four vector which can be associated with the motion of the heavy particles is the Dirac current

$$\zeta_i = \psi^*\alpha\psi; \quad (\alpha_{1,2,3} = \text{Dirac matrices}, \alpha_4 = \delta_{ik}).$$

According to Gordon,[3] ζ can be resolved into two parts, *viz.*, the convection current

$$j_k = \frac{\hbar}{2Mi}\left(\psi^*\beta\frac{\partial\psi}{\partial x^k} - \psi\beta^*\frac{\partial\psi^*}{\partial x^k}\right)$$

and the polarization current

$$j'_k = \frac{\hbar}{2Mi}\frac{\partial M_{k\mu}}{\partial x_\mu}; \quad M_{k\mu} = \psi^*\beta\alpha_k\alpha_\mu\psi,$$

each of them separately satisfying the continuity equation

$$\partial j_\mu/\partial x_\mu = 0.$$

A general wave equation would therefore be,

$$\frac{\partial^2\phi_i}{\partial x_\mu \partial x^\mu}-\kappa^2\phi_i=-\frac{4\pi}{c}(\gamma_1 j_i+\gamma_2 j'_i)$$

with γ_1 and γ_2 as independent constants.

This together with the wave equation for the free heavy particles defines practically uniquely a Lagrangian and Hamiltonian in which the interaction heavy particle-meson field is represented by:

$$-W=\frac{\gamma_1}{c}\phi_\mu j^\mu+\frac{\gamma_2\hbar}{4Mci}\left(\frac{\partial\phi^\nu}{\partial x_\mu}-\frac{\partial\phi^\mu}{\partial x_\nu}\right)M_{\mu\nu}.$$

Proceeding to the non-relativistic limit for the heavy particles, neglecting terms $\sim v/c$ and leaving out δ-functions, one gets in the usual way the interaction potential:

$$V=\left\{\gamma_1^2+\gamma_2^2\left(\frac{\hbar\kappa}{2Mc}\right)^2\left[\left(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2-\frac{(\boldsymbol{\sigma}_1\cdot\mathbf{r})(\boldsymbol{\sigma}_2\cdot\mathbf{r})}{r^2}\right)+\left(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2-\frac{3(\boldsymbol{\sigma}_1\cdot\mathbf{r})(\boldsymbol{\sigma}_2\cdot\mathbf{r})}{r^2}\right)\left(\frac{1}{\kappa r}+\frac{1}{\kappa^2r^2}\right)\right]\right\}\frac{e^{-\kappa r}}{r}.$$

With $\gamma_1=g_1$, $\gamma_2=(2M/\mu)g_2$, (μ = meson mass) this is the form given by Youkawa *et al.*

If we take $\gamma_1=\gamma_2=e$ and let $\kappa\to 0$, this expression changes continually into its electrostatic counterpart

$$V_{\text{el}}=\frac{e^2}{r}+\left(\frac{e\hbar}{2Mc}\right)^2\frac{(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2)r^2-3(\boldsymbol{\sigma}_1\cdot\mathbf{r})(\boldsymbol{\sigma}_2\cdot\mathbf{r})}{r^5};$$

that is, the Coulomb interaction + the spin-spin interaction which follows from Breit's operator in non-relativistic approximation.

From the point of view proposed above one would expect $\gamma_1=\gamma_2$ also in meson theory, thus leaving only one constant free for each sort of field. Only tnen will the difference between electrodynamics and meson theory merely come from the finite rest mass of the mesons. On account of the conservation of the currents it is of course formally possible to choose $\gamma_1\neq\gamma_2$, but this is a separate assumption which cannot be inferred from the analogy with electrodynamics.

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On the Gyromagnetic Effects in Ferromagnetic Substances

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September 16, 1941

THE refined researches of Barnett and others[1] on the gyromagnetic effects in ferromagnetic substances have revealed positive deviations of the ratio ρ of mechanical to magnetic moment from the spin-only value mc/e. This obviously means that, besides the spins, the orbital motion of electrons also contributes to the mechanical and magnetic moments. But further understanding was blocked by the apparent influence of minor structural differences in the samples upon the magnitude of the deviation. The most striking example was that the deviation mentioned for Yensen electrolytic iron, as observed in the Barnett effect, was three times larger than that for soft Armco or Norway iron. Even more incomprehensible was the difference between the gyromagnetic ratio ρ for Yensen iron and also for an iron-cobalt alloy, observed in the Barnett effect, and the lower gyromagnetic ratio observed in the Einstein - de Haas effect for the same substances.

Now Barnett recently in a footnote[2] sheds doubt upon his own former results on the Barnett effect of Yensen iron and the iron-cobalt alloy, mentioning that a redetermination appears to give much lower values of ρ, in agreement with those obtained in the Einstein - de Haas effect. It is the purpose of this note to point out that this considerably simplifies the situation. Considering Barnett's results and omitting the doubtful data, one sees that the ρ-values seem to split into four different groups, namely, nickel and the alloys containing mainly nickel, cobalt and the alloys consisting primarily of cobalt, iron and the alloys containing mainly iron, and finally Heusler's alloy. The approximate values of $\rho e/mc$ for each group will be found in Table I.

TABLE I.

SUBSTANCES	$\rho e/mc$ EXP	$\rho e/mc$ CALC.	ION
Heusler's alloy	1.01	1.00	Mn^{++}
Iron and alloys	1.03	1.07–1.11	Fe^{++}
Cobalt and alloys	1.08	1.12–1.27	Co^{++}
Nickel and alloys	1.05	1.13–1.18	Ni^{++}

On the other hand, recently the gyromagnetic ratios of bivalent paramagnetic salts have been calculated[3] from the deviations of their susceptibilities from the spin-only values. In the right-hand side of the table these calculated values of $\rho e/mc$ are given.

Apparently there is a parallelism between the two series of numbers, though the theoretical paramagnetic deviations from unity are about three times larger than the experimental ferromagnetic deviations. Does this mean that the ions responsible for ferromagnetism are doubly ionized and subject to an interaction with their surroundings which is similar to (though a few times larger than) that characteristic of the bivalent ions in paramagnetic salts?

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